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Relative Reactivities Of Some Metal-metal Bonded Compounds

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RELATIVE REACTIVITIES OF SOME METAL-METAL BONDED COMPOUNDS

by

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ABSTRACT

The reactions of trimethyltin(cyclopentadienyl)iron dicarbonyl and its silicon and germanium analogues with a variety of reagents have been studied. Chlorine, iodine monochloride, and trifluoroiodomethane cleaved all three metal-metal bonds, whereas hydrogen chloride cleaved the silicon-iron and germanium-iron bonds, but cleaved the tin-carbon bond in the tin-iron compound.

The three metal-metal bonded compounds formed a number of stable insertion products. Although the silicon-iron compound did not react with sulfur dioxide, the germanium-iron compound formed a simple insertion product. The tin-iron compound reacted with sulfur dioxide to form a complex, polymeric product.

All three compounds formed insertion products with hexafluorobut-2-yne. The tin-iron compound reacted with hexafluorobut-2-yne to give a product which suggested that a compound containing two molecules of hexafluorobut-2-yne to one of the metal-metal bonded compound had been formed.

Both the silicon-iron and germanium-iron compound formed an insertion product with 3,3,3-trifluoropropyne. The tin-iron compound did not form an insertion product with this

reagent.

Neither trimethyltin(cyclopentadienyl)iron dicarbonyl nor its silicon or germanium analogues reacted with trifluoroethylene, chlorotrifluoroethylene, or perfluorocyclobutene.

TO MY WIFE

AGNES

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CHAPTER I

INTRODUCTION

Research into the phenomenon of metal-metal bonding began many years ago (1). Recent reviews (2,3) have attempted to cover the many different metal-metal bonded systems, and the various methods of synthesis. The most general synthetic routes are:

1) metathetical reactions between a metal anion and a metal halide (4):

$$NaFe(CO)_2(\pi\text{-}C_5H_5) + (CH_3)_3SnCl \longrightarrow (CH_3)_3SnFe(CO)_2(\pi\text{-}C_5H_5) + NaCl$$

2) elimination of a hydrogen halide from a metal halide and a metal hydride (5):

$$ClFe(CO)_2(\pi\text{-}C_5H_5) + HGeCl_3 \longrightarrow Cl_3GeFe(CO)_2(\pi\text{-}C_5H_5) + HCl$$

3) insertion of a Group IVA metal dihalide into a metal-metal or a metal-halide bond (6,7):

$$\left[(\pi\text{-}C_5H_5)Fe(CO)_2\right]_2 + GeI_2 \longrightarrow I_2Ge\left[Fe(CO)_2(\pi\text{-}C_5H_5)\right]_2$$

$$(\pi\text{-}C_5H_5)Fe(CO)_2Cl + SnCl_2 \longrightarrow (\pi\text{-}C_5H_5)Fe(CO)_2SnCl_3$$

4) oxidative addition of a metal halide to a transition

metal compound (8):

$$SnCl_4 + Fe(CO)_5 \longrightarrow (Cl_3Sn)Fe(CO)_4Cl$$

Clearly, compounds with Group IV elements (silicon, germanium, tin and lead) bonded to transition metals must now be regarded as well known. Less is known of the reactivity of the metal-metal bond or the two different metal-carbon bonds in compounds of this type.

Obviously, in a general compound

$$R_3M\text{-}M'(CO)_x$$

the favored site for reaction is a function of the two metals involved, and is also a function of the group "R". Indeed, the correlation of results from compounds involving different transition metals (M') is difficult. Prediction of the reactions of one of these compounds based upon the reactions of another is even more difficult.

To gain insight into the reaction of metal-metal bonded compounds, it is necessary to study compounds containing transition metals from as many triads as possible.

Thus far, reactions of hydrogen halides, halogens (9,10), trifluoroiodomethane (9,11), and fluorinated derivatives of ethylene (9,11,12) have been studied for the systems trimethyltinmanganese pentacarbonyl and trimethyltincobalt tetracarbonyl.

The reactions of triphenyltinmanganese pentacarbonyl and the various chloromethyltin derivatives of manganese pentacarbonyl are much more limited in scope than those of trimethyltinmanganese pentacarbonyl (9).

Fluoro-olefins insert into the metal-metal bond in trimethylgermaniummanganese pentacarbonyl, but the products from reaction with an unsymmetric olefin may be very different from those for the corresponding reaction of trimethyltinmanganese pentacarbonyl (13).

$$(CH_3)_3GeMn(CO)_5 + C_2F_3Cl \longrightarrow (CH_3)_3GeCF=CF_2 + [Mn(CO)_4Cl]_2$$

$$(CH_3)_3SnMn(CO)_5 + C_2F_3Cl \longrightarrow (CH_3)_3SnCl + (CH_3)_3SnF + CF_2=CFCOMn(CO)_5 + Cl(F)C=C(F)Mn(CO)_5$$

The reactivity of these compounds containing the tin-manganese bond is clearly dependent on the substituents on the tin atom. The differing reactivity of trimethylgermaniummanganese pentacarbonyl and trimethyltinmanganese pentacarbonyl demonstrates that the nature of the metal-metal bond is altered by changing the Group IV metal. This alteration is a function of the inductive and π-acceptor properties of the Group IV atom, in combination with its substituents.

It was decided to study the reactions of the three compounds; trimethylsilicon-, trimethylgermanium-, and trimethyltin(cyclopentadienyl)iron dicarbonyl. The effect of changing the Group IV metal on the reactivity of the metal-metal bond to another transition metal may thus be studied, while all other possible variables are kept constant. Reactions of unsymmetrical electrophilic reagents (hydrogen chloride, iodine monochloride) and unsymmetrical fluoro-olefins may then provide information about the polarity of

the metal-metal bond, and the nature of the mechanism. If a reaction involving a metal-metal bond and a polar reagent proceeds through a four-centered transition state, the products should contain the most "electron-rich" species attached to, or nearest the same metal in most cases. Reactions proceeding by a dissociative mechanism could perhaps be interpreted as reaction of the cyclopentadienyl iron dicarbonyl anion, reactions well characterized at least in the case of fluoro-olefins (14,15). Similarly, the reactions of the trimethyltin radical with fluoro-olefins have been extensively studied (16,17).

Thus, reactions of these compounds with selected reagents may provide information about the bond between a Group IVA metal and iron, as well as the nature of the reaction mechanism.

CHAPTER II

CLEAVAGE REACTIONS OF METAL-METAL BONDED COMPOUNDS

A: Reactions of Metal-Metal Bonded Compounds with Halogens

Introduction

The halogenation reactions of metal-metal bonded compounds containing a Group IVA metal and a Group VIIB metal are listed in Table I. In general, phenylated tin compounds undergo metal-carbon bond scission. Gorsich (4) showed that the chlorination of bis (pentacarbonyl manganese) diphenyltin involved cleavage of the metal-carbon bond, followed by cleavage of the metal-metal bond.

$$(C_6H_5)_2Sn\left[Mn(CO)_5\right]_2 + 2Cl_2 \longrightarrow Cl_2Sn\left[Mn(CO)_5\right]_2 + 2C_6H_5Cl$$

$$Cl_2Sn\left[Mn(CO)_5\right]_2 + Cl_2 \longrightarrow Cl_3SnMn(CO)_5 + ClMn(CO)_5$$

The metal-metal bond in trichlorotinmanganese pentacarbonyl was stable to chlorine.

In contrast, bromination of bis (pentacarbonyl manganese)diphenylgermanium cleaved the metal-metal bond (19).

$$(C_6H_5)_2Ge\left[Mn(CO)_5\right]_2 + 2Br_2 \longrightarrow (C_6H_5)_2GeBr_2 + 2BrMn(CO)_5$$

Chlorination of triphenylgermaniummanganese pentacarbonyl

TABLE I

REACTIONS OF METAL-METAL-BONDED COMPOUNDS WITH HALOGENS AND HYDROGEN HALIDES

Metal-Metal Bonded Compounds	Halogen Cleaves	ref	H-X Cleaves	ref
$(C_6H_5)_3SnMn(CO)_5$	M-C (Cl_2)	4	M-C (HCl)	4
$Cl_3SnMn(CO)_5$	no reaction (Cl_2)	4	no reaction (HCl)	4
$(CH_3)_3SnMn(CO)_5$	M-M (Cl_2)	9,21	M-C (HCl,HBr,HI)	9,21
$(C_6H_5)_2Sn[Mn(CO)_5]_2$	M-C (Cl_2) M-M	4		
$(C_6H_5)_3SnRe(CO)_5$	M-C (Cl_2)	18	M-C (HCl)	18
$(C_6H_5)_2Sn[Re(CO)_5]_2$	M-C (Br_2)	18		
$(C_6H_5)_3GeMn(CO)_5$	M-C,M-M (Br_2) M-C (Cl_2)	19	no reaction (HCl)	19
$(C_6H_5)_2Ge[Mn(CO)_5]_2$	M-M (Br_2)	19		
$(C_6H_5)_3GeRe(CO)_5$	M-C (Br_2)	20		
$(C_6H_5)_2Ge[Re(CO)_5]_2$	M-M (Br_2)	20	M-C (HCl)	20
$(CH_3)_3GeMn(CO)_5$			no reaction (HCl)	22

did give metal-carbon bond cleavage, however.

The mean dissociation energies of the metal-carbon bonds in the tetramethyl compounds of silicon, germanium and tin are given as 65, 61 and 50 Kcal, respectively (25). The values for the corresponding tetraphenyl compounds are given as 73, 67 (estimated) and 54 Kcal, respectively (26). On the basis of these average bond energies, it is expected that the germanium-carbon bond will be less likely to undergo cleavage than the tin-carbon bond. In the reaction of the three tetraethyl compounds with chlorine, this order is observed (27). Tetraethylsilane undergoes chlorination on the hydrocarbon chain, tetraethylgermane is cleaved to give triethylchlorogermane and chloroethane, and tetraethyltin is readily converted by chlorine to diethyltin dichloride.

For the compounds in Table I, the germanium-carbon bond is more stable to attack by halogen than the germanium-metal bond. The opposite appears to be true for the corresponding tin compounds. However, the metal-metal bond in trimethyltinmanganese pentacarbonyl is cleaved by chlorine (9,21). Thus the tin-carbon bond is more resistant to cleavage by halogen in the methylated derivatives of tin than in the phenylated derivatives.

Halogenation reactions of other compounds involving bonds between transition metals and tin or germanium are listed in Table II. Metal-metal bond cleavage is the preferred reaction for both tin and germanium derivatives.

TABLE II

REACTIONS OF METAL-METAL BONDED COMPOUNDS WITH HALOGENS AND HYDROGEN HALIDES

Metal-Metal Bonded Compounds	Halogen Cleaves	ref	H-X Cleaves	ref
$(C_6H_5)_3SnMo(CO)_3Cp$[a]			M-C (HCl)	22
$(C_6H_5)_3SnW(CO)_3Cp$			M-C (HCl)	22
$(CH_3)_3SnMo(CO)_3Cp$	M-M (Cl_2,I_2)	22	M-C (HCl)	22
$(CH_3)_3SnW(CO)_3Cp$	M-M (Cl_2,I_2)	22	M-C (HCl)	22
$(CH_3)_3GeMo(CO)_3Cp$	M-M (Cl_2)	23	M-M (HCl)	23
$(C_6H_5)_3SnCo(CO)_4$	M-M (Cl_2)	10	M-M (HCl)	10
$(CH_3)_3SnCo(CO)_4$	M-M (Cl_2)	10,21	M-M (HCl)	10,21
$(C_6H_5)_3SnFe(CO)_2Cp$	M-M (Cl_2)	4	M-C (HCl)	4
$(C_2H_5)_3GeFe(CO)_2Cp$	M-M (Br_2)	24		
$(CH_3)_3SnFe(CO)_2Cp$	M-M (Cl_2,I_2)	b	M-C (HCl)	b
$(CH_3)_3GeFe(CO)_2Cp$	M-M (Cl_2)	b	M-M (HCl)	b
$(CH_3)_3SiFe(CO)_2Cp$	M-M (Cl_2)	b	M-M (HCl)	b

a Cp = (π-C_5H_5)

b this work

Results and Discussion

The choice of solvent for the chlorination of metal-metal bonded compounds containing iron is important. The reported instability (4,18,24) of the cyclopentadienyl iron dicarbonyl halides toward excess halogen is possibly a result of the use of carbon tetrachloride as solvent for these reactions. In this study, consistently poor results were obtained for cleavage reactions carried out in carbon tetrachloride.

Chlorination of trimethyltin(cyclopentadienyl)iron dicarbonyl led to metal-metal bond cleavage. A red solution of cyclopentadienyl iron dicarbonyl chloride resulted immediately upon melting of the solvent.

$$(CH_3)_3SnFe(CO)_2(\pi\text{-}C_5H_5) + Cl_2 \longrightarrow (CH_3)_3SnCl + ClFe(CO)_2(\pi\text{-}C_5H_5)$$

A considerable amount of intractable white solid was produced when the reaction was carried out in carbon tetrachloride. The reaction proceeded smoothly in hexane at -78°, although not all of the metal-metal bonded compound was consumed. Reaction at low temperature and in the dark should have minimized reaction of chlorine with solvent.

Iodination of trimethyltin(cyclopentadienyl)iron dicarbonyl in refluxing carbon tetrachloride led to considerable decomposition and to the production of trimethyltin chloride. Iodination proceeded smoothly in hexane at 60° to give trimethyltin iodide and cyclopentadienyl iron dicarbonyl iodide.

Chlorination of trimethylgermanium(cyclopentadienyl)-iron dicarbonyl and trimethylsilicon(cyclopentadienyl)iron dicarbonyl proceeded at low temperature in hexane with cleavage of the metal-metal bond.

The polar interhalogen, iodine monochloride, could give rise to cleavage products corresponding to a specific orientation:

$$(CH_3)_3SnFe(CO)_2(\pi\text{-}C_5H_5) + ICl \begin{cases} \nearrow (CH_3)_3SnI + ClFe(CO)_2(\pi\text{-}C_5H_5) \\ \searrow (CH_3)_3SnCl + IFe(CO)_2(\pi\text{-}C_5H_5) \end{cases}$$

The reaction of iodine monochloride with trimethyltin-(cyclopentadienyl)iron dicarbonyl resulted in incomplete consumption of the metal-metal bonded compound. Although both trimethyltin chloride and trimethyltin iodide were produced, only cyclopentadienyl iron dicarbonyl iodide was isolated. It appears that the positive end of an attacking dipole becomes attached to the iron atom. Booth (9) found that the reaction of trimethyltinmanganese pentacarbonyl with iodine monochloride gave manganese pentacarbonyl iodide and a mixture of trimethyltin iodide and trimethyltin chloride.

Similar results were obtained for reactions with trimethylgermanium(cyclopentadienyl)iron dicarbonyl. The metal-metal bonded compound was not always completely consumed. Although only cyclopentadienyl iron dicarbonyl

iodide was isolated, both trimethylchlorogermane and trimethyliodogermane were produced.

Cleavage of trimethylsilicon(cyclopentadienyl)iron dicarbonyl was selective. Only cyclopentadienyl iron dicarbonyl iodide and trimethylchlorosilane were isolated.

In the reaction of iodine monochloride with trimethyltin(cyclopentadienyl)iron dicarbonyl, there was evidence of tin-carbon bond cleavage. The lower energy of the tin-carbon bond probably accounts for these side reactions which were not observed in the silicon and germanium compounds.

Assuming that the effective electronegativity of the iron moiety is the same in all three compounds under study, the polarity of the metal-metal bonds should be a function of the size and electronegativity of the silicon, germanium, and tin atoms. The electronegativities of these atoms have been determined by Allred and Rochow (28,29) to be 1.90, 2.01, and 1.96, respectively. The corresponding covalent radii are 1.17, 1.22, and 1.41 angstroms, respectively (30).

Unfortunately, the "size" of the iron atom in these compounds is unknown. The length of the tin-iron bond in triphenyltin(cyclopentadienyl)iron dicarbonyl is 2.53 angstroms (31) and the length in bis (cyclopentadienyl iron dicarbonyl)dimethyltin is 2.60 angstroms (32), implying that the covalent radius of the iron atom is about 1.18 angstroms, or approximately the same as that for the silicon

and germanium atoms.

The direction of cleavage in the iodine monochloride reactions indicates that the charge separation in the metal-metal bonds is

$$\overset{\delta+}{M}\text{---}\overset{\delta-}{Fe} \qquad M=Si,\ Ge,\ Sn$$

On the basis of electronegativity considerations, the germanium-iron bond should be less polar than the silicon-iron and tin-iron bonds. Only the silicon-iron bond is selectively cleaved by iodine monochloride. Either the silicon-iron bond is the most polar bond, or the mixed halides of tin and germanium are produced by some unknown exchange mechanism. Perhaps the small size of the silicon atom favors a more selective arrangement of a four-centered transition state such as

$$\overset{\delta+}{Si}\text{---}\overset{\delta-}{Fe}$$

$$\overset{\delta-}{Cl}\text{---}\overset{\delta+}{I}$$

B: Reactions of Metal-Metal Bonded Compounds with Hydrogen Chloride

Introduction

Reactions with hydrogen chloride, a polar reagent, may also give rise to products corresponding to a particular charge orientation during cleavage.

The reactions of a number of metal-metal bonded compounds

with hydrogen chloride are listed in Tables I, II, and III. As in the halogenation reactions, metal-carbon bond cleavage is more likely for the tin compounds than for the corresponding germanium analogues. Although metal-carbon bond cleavage occurs with bis (pentacarbonyl rhenium) diphenylgermanium, most germanium-containing compounds undergo metal-metal bond scission.

Triphenylgermaniummanganese pentacarbonyl and trimethylgermaniummanganese pentacarbonyl do not react with hydrogen chloride. It appears that the compounds in the tables which contain manganese (and rhenium) are the most resistant to cleavage by hydrogen chloride or halogens, Indeed, silylmanganese pentacarbonyl undergoes hydrogen replacement, not metal-metal bond cleavage (37).

$$H_3SiMn(CO)_5 + 2HCl \longrightarrow H_{3-x}Cl_xSiMn(CO)_5 + xH_2$$

Silylcobalt tetracarbonyl (38) and bis silyliron tetracarbonyl (39) react with hydrogen chloride with metal-metal bond scission.

$$H_3SiCo(CO)_4 + HCl \longrightarrow H_3SiCl + HCo(CO)_4$$

Stepwise replacement of the methyl groups on tin occurs in the reaction of trimethyltinmanganese pentacarbonyl and trimethyltin(cyclopentadienyl)molybdenum tricarbonyl and its tungsten analogue (9,22).

$$(CH_3)_3SnMn(CO)_5 + HCl \longrightarrow Cl(CH_3)_2SnMn(CO)_5 + CH_4\uparrow$$

$$Cl(CH_3)_2SnMn(CO)_5 + HCl \longrightarrow Cl_2(CH_3)SnMn(CO)_5 + CH_4\uparrow$$

Replacement of a single methyl group is not easily controlled, but replacement of more than two does not occur.

TABLE III

REACTIONS OF METAL-METAL BONDED COMPOUNDS WITH HYDROGEN HALIDES

Metal-Metal Bonded Compound	Hydrogen Halide Cleaves	ref
$(\pi\text{-}C_5H_5)_2ZrCl\ Si(C_6H_5)_3$	M-M (HCl)	33
$(C_6H_5)_3PAuGe(C_6H_5)_3$	M-M (HCl)	34
$[(C_2H_5)_3P]_2Pt(Cl)Si(CH_3)_3$	M-M (HCl)	35
$[(C_2H_5)_3P]_2Pt(Cl)Ge(CH_3)_3$	M-M (HCl)	35
$[(C_2H_5)_3P]_2Pt(C_6H_5)Ge(CH_3)_3$	M-M (HCl)	35
$[(C_2H_5)_3P]_2Pt\ Pb(C_6H_5)_3\ 2$	M-M (HCl)	36

As mentioned before, trimethylgermaniummanganese pentacarbonyl does not react with hydrogen chloride. With trimethylgermanium(cyclopentadienyl)molybdenum tricarbonyl and its tungsten analogue, metal-metal bond cleavage occurs (22). The stability of the three germanium compounds is comparable to that of their tin analogues (40,41). Metal-carbon bond cleavage occurs more readily in metal-metal bonded compounds containing tin than in the corresponding germanium analogues because the tin-carbon bond is weaker than the germanium-carbon bond (32).

In both trimethyltincobalt tetracarbonyl and triphenyltincobalt tetracarbonyl, hydrochlorination produces metal-metal bond cleavage (10). Although the metal-metal bond is relatively stable thermally, there is evidence for the intermediacy of the cobalt tetracarbonyl anion in the reactions of these compounds in polar solvents (11). Perhaps the tin-cobalt bond is more polarizable than the tin-manganese bond, and metal-metal bond cleavage occurs more readily than metal-carbon bond cleavage in both compounds containing the tin-cobalt bond.

The metal-metal bonded compounds in Table III react with hydrogen chloride to give metal-metal bond cleavage in the "opposite" direction.

$$(C_6H_5)_3PAuGe(C_6H_5)_3 + HCl \longrightarrow (C_6H_5)_3PAuCl + HGe(C_6H_5)_3$$

Thus it appears that the polarity of the metal-metal bond in these compounds is

$$\overset{\delta-}{M}—\overset{\delta+}{M'}$$

M= Si, Ge

M'= Au, Zr

Since the metal-metal bond cleavage in platinum compounds proceeds by elimination from the six-coordinate hydrogen chloride adduct (35), the observed products do not imply that the metal-metal bond in platinum compounds is polarized in the above manner.

Results and Discussion

Both trimethylgermanium(cyclopentadienyl)iron dicarbonyl and trimethylsilicon(cyclopentadienyl)iron dicarbonyl undergo metal-metal bond cleavage with hydrogen chloride.

$$(CH_3)_3MFe(CO)_2(\pi\text{-}C_5H_5) + HCl \longrightarrow (CH_3)_3MCl + HFe(CO)_2(\pi\text{-}C_5H_5)$$

where M= Si or Ge.

When hydrogen chloride is bubbled through a solution of trimethyltin(cyclopentadienyl)iron dicarbonyl in dichloromethane, one methyl group is replaced.

$$(CH_3)_3SnFe(CO)_2(\pi\text{-}C_5H_5) + HCl \longrightarrow Cl(CH_3)_2SnFe(CO)_2(\pi\text{-}C_5H_5) + CH_4\uparrow$$

If the reaction is carried out in a sealed tube, methane may be detected spectroscopically.

Unfortunately, the nature of the reaction of chlorodimethyltin(cyclopentadienyl)iron dicarbonyl with hydrogen chloride is unclear. Cleavage of the metal-metal bond in the manner of the silicon and germanium compounds does not occur.

$$Cl(CH_3)_2SnFe(CO)_2(\pi\text{-}C_5H_5) + HCl \longrightarrow (CH_3)_2SnCl_2 + HFe(CO)_2(\pi\text{-}C_5H_5)$$

Although cyclopentadienyl iron dicarbonyl hydride was isolated, no dimethyltin dichloride was found. However, this reaction may be reversible. Spectroscopic investigation of the crude product of the reaction indicated a multitude of reaction products. A reaction of sufficient scale to permit isolation of these products was not attempted.

Again, cleavage of methyl groups from tin occurs more readily than cleavage from silicon or germanium. The products of cleavage with the silicon and germanium compounds suggest a four-centered transition state

$$(CH_3)_3M\cdots Fe(CO)_2(\pi\text{-}C_5H_5)$$
$$\quad\;\; Cl\cdots H$$

C: Reactions of Metal-Metal Bonded Compounds with Trifluoroiodomethane

Introduction

A radical chain mechanism was proposed for the reaction of trifluoroiodomethane with hexamethylditin, giving trimethyltin iodide and trifluoromethyltrimethyltin (42). Apparently only the radical $I^{\bullet}$ reacted with trimethyltinmanganese pentacarbonyl when that compound was irradiated in the presence of trifluoroiodomethane (9).

$$(CH_3)_3SnMn(CO)_5 + 2CF_3I \longrightarrow (CH_3)_3SnI + IMnCO_5 + C_2F_6$$

Reaction of trimethyltincobalt tetracarbonyl with

trifluoroiodomethane under thermal conditions produced equal amounts of trimethyltin iodide and trimethyltin fluoride, and fluorinated derivatives of tricobalt nonacarbonyl (11).

In neither of the above two examples was there evidence for specific cleavage by a polar reagent

$$CF_3\overset{\delta-}{}\!\!-\!\!\overset{\delta+}{}I$$

Results and Discussion

The reaction of trimethyltin(cyclopentadienyl)iron dicarbonyl with excess trifluoroiodomethane under mild thermal conditions produced nearly equal amounts of trimethyltin iodide and trimethyltin fluoride. As in the reaction of trimethyltincobalt tetracarbonyl, no trifluoromethyltrimethyltin was found although it should be stable at the reaction temperature (42). Slightly more cyclopentadienyl iron dicarbonyl iodide was formed than trifluoromethyl(cyclopentadienyl)iron dicarbonyl. Difficulty in the separation of these two compounds prevented determination of their exact ratio.

Cleavage of trimethylgermanium(cyclopentadienyl)iron dicarbonyl by trifluoroiodomethane was non-selective.

$$(CH_3)_3GeFe(CO)_2(\pi\text{-}C_5H_5) + 2CF_3I \longrightarrow (CH_3)_3GeF + (CH_3)_3GeI + IFe(CO)_2(\pi\text{-}C_5H_5) + CF_3Fe(CO)_2(\pi\text{-}C_5H_5)$$

Again, the known compound trifluoromethyltrimethylgermane

was not isolated (43).

Cleavage of trimethylsilicon(cyclopentadienyl)iron dicarbonyl proceeded more selectively. Only trimethylfluorosilane and cyclopentadienyl iron dicarbonyl iodide were produced.

Conclusions

A cyclic four-centered intermediate is proposed for the iodination of hexaphenylditin in cyclohexane (44). Hydrochlorination and halogenation of tetra-alkyl tin compounds in non-donor solvents also involves a four-centered transition state (45).

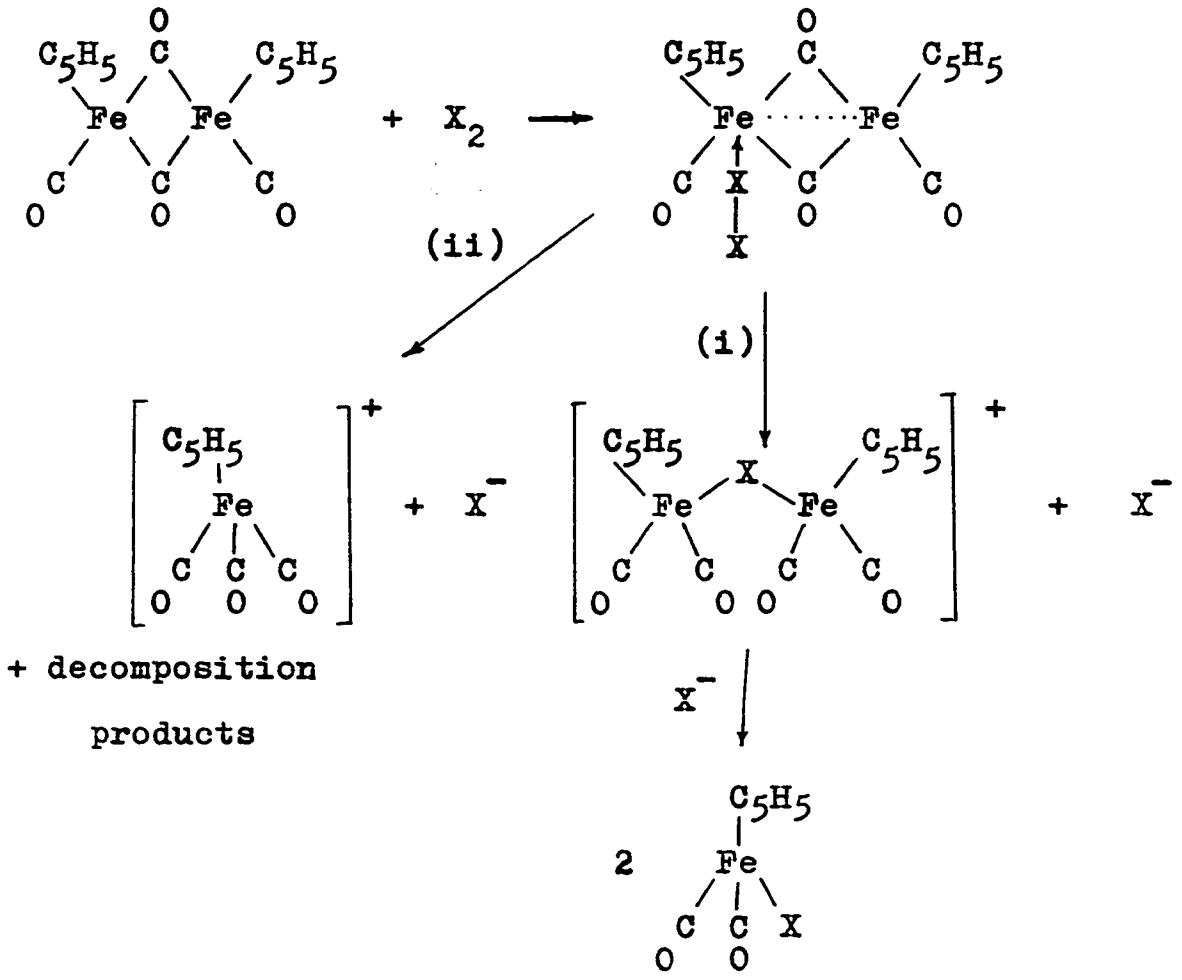
The iodination of dimanganese decacarbonyl in solution has been studied kinetically. The reaction with iodine follows the formation of a reactive intermediate, such as $(OC)_5Mn\cdot$ radical pairs or a bridged species

$$(OC)_4Mn(\overset{O}{\overset{\|}{C}})Mn(CO)_5 \quad \text{(46)}.$$
$$\qquad\qquad\quad I—I$$

Results of a similar study favor the bridged species as the reactive intermediate in the iodination of dirhenium decacarbonyl (47).

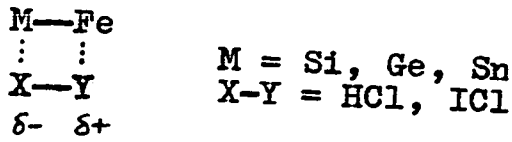
Iodination of cyclopentadienyl iron dicarbonyl dimer in benzene proceeds through the ionic intermediate $\left[(\pi\text{-}C_5H_5)Fe(CO)_2\right]_2I^+$ (48). In methylene chloride solution, this intermediate reacts with any halide ion. The inter-

halogens, iodine monochloride and iodine monobromide, both give rise to the same bridged iodo compound. During chlorination of the iron dimer, ionic species such as $(\pi\text{-}C_5H_5)Fe(CO)_3^+$ are formed. Two mechanistic pathways are proposed which involve (i) ultimate symmetric cleavage and (ii) ultimate asymmetric cleavage of the bridged compound



It is interesting to speculate on the mechanism of the cleavages reported here. Halogenations carried out in hexane are unlikely to be solvent assisted and could easily involve a four-centered transition state. However, a non-cyclic transition state is not excluded. The same arguments

apply to the hydrochlorination reactions. The charge orientation in such a transition state appears to be



It must be stressed that this discussion is based only on stoichiometric grounds.

No intermediate corresponding to that observed by Haines and du Preez (48) was detected. The dichloromethane extract of the halogenation reaction products was cyclopentadienyl iron dicarbonyl halide. The dichloromethane-insoluble residues were quite intractable. Even where it was possible to mull these residues, the infrared spectra did not contain any peaks characteristic of the metal-metal bonded compounds.

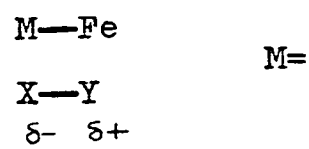
The reactions with trifluoroiodomethane, which also functioned as solvent, were not subject to the same restrictions. The solvent properties of trifluoroiodomethane are not known. The absence of selectivity in these reactions suggests that if a four-centered transition state was involved, there was no preferred orientation of the pseudo-halogen in the transition state. Equal yields of all the cleavage products were isolated for the reactions of the tin-iron and germanium -iron bonds with trifluoroiodomethane. The trimethyltin fluoride and trimethylfluorogermane may have resulted from fluorine abstraction from trifluoro-

iodomethane, rather than from decomposition of the corresponding trifluoromethyl compounds.

The selectivity of the reaction of the silicon-iron bond with trifluoroiodomethane may have been due to the high affinity of silicon for fluorine, as demonstrated by the ready elimination of ∝-fluorine from fluorinated silicon compounds (49). This affinity, coupled with the slightly smaller size of the silicon atom, may have permitted abstraction of fluorine from any approaching trifluoroiodomethane. The reaction of bis (trimethylsilyl)mercury with trifluoroiodomethane (50) also selectively produces trimethylfluorosilane (and mercuric iodide).

The cleavage reactions with trifluoroiodomethane demonstrates a definite order of reactivity. The reactivity of the silicon-iron bond is less than that of the germanium-iron bond which is less than that of the tin-iron bond. The halogenation reactions of the three metal-metal bonds all proceed under the same mild conditions.

Certainly, the results of cleavage reactions of the three metal-metal bonded compounds studied can be reconciled with a four-centered transition state (which need not be cyclic), although the evidence is far from conclusive. The charge orientation in the suggested transition state is



M= Si, Ge, Sn

This implies that the metal-metal bond is polarized (or at least polarizable) in the manner

$$M^{\delta+}—Fe^{\delta-} \qquad M= Si, Ge, Sn.$$

The cleavage reactions indicate that the silicon-iron bond is more polar than the germanium-iron or tin-iron bonds.

CHAPTER III

REACTION OF METAL-METAL BONDED COMPOUNDS WITH SULFUR DIOXIDE

Introduction

Following the original observation of sulfur dioxide insertion into metal-carbon bonds (51), many sulfinates with both sulfur and oxygen bound to the metal have been reported (52, 53, 54). Insertion into transition metal-to-carbon bonds usually produces S-sulfinates, even when insertion is accompanied by rearrangement (55).

$$(\pi\text{-}C_5H_5)Fe(CO)_2R + SO_2 \longrightarrow (\pi\text{-}C_5H_5)Fe(CO)_2\text{-}\overset{O}{\overset{\|}{S}}\text{-}\overset{O}{\overset{\|}{}}\text{-}R$$

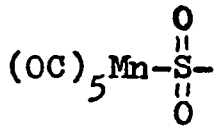
$$(OC)_5Mn\text{-}CH_2C{\equiv}CH + SO_2 \longrightarrow (OC)_5Mn\text{-}\overset{O}{\overset{\|}{S}}\text{-}OCH_2C{\equiv}CH$$

Organomercury compounds react with sulfur dioxide giving products which exhibit either sulfur or oxygen bound to the metal (53). In the case of diphenylmercury, the insertion is reversible (56).

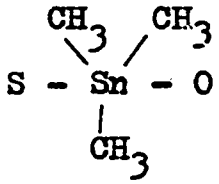
$$C_6H_5HgSO_2(C_6H_5) \rightleftharpoons (C_6H_5)_2Hg + SO_2$$

Insertion of sulfur dioxide into metal-metal bonds has also been demonstrated to occur. The tin-tin and tin-manganese bonds react with sulfur dioxide to afford products containing varying amounts of sulfur dioxide (57).

In the compound $(CH_3)_3SnMn(CO)_5l \cdot 5SO_2$, both the group



and the group



are indicated from spectroscopic data. The structure is unknown, but all the evidence is consistent with metal-metal bond cleavage.

It is also possible to insert sulfur dioxide into a metal-carbon bond in a metal-metal bonded compound (58).

$$(C_6H_5)_2Sn\left[Fe(CO)_2(\pi\text{-}C_5H_5)\right]_2 + SO_2 \longrightarrow (C_6H_5SO_2)_2Sn\left[Fe(CO)_2(\pi\text{-}C_5H_5)\right]_2$$

Structural analysis shows that this compound contains C-S(O)-O-Sn units, and has intact metal-metal bonds (59).

In view of these two different possibilities, metal-metal or metal-carbon bond insertion, it was of much interest to examine the behavior of the three compounds with silicon-

iron, germanium-iron, and tin-iron bonds with sulfur dioxide.

Results and Discussion

Reaction of trimethyltin(cyclopentadienyl)iron dicarbonyl with liquid sulfur dioxide gave a glassy product of empirical formula $C_{28}H_{28}O_{10}S_3Fe_2Sn_2$, corresponding to a product of composition $(CH_3)_3SnFe(CO)_2(\pi\text{-}C_5H_5)1.5SO_2$, analogous to the compound $(CH_3)_3SnMn(CO)_5 1.5SO_2$ (57). Again, more than one mole of sulfur dioxide was incorporated per mole of metal-metal bonded compound. Thus the products are not simply $M\text{-}S(O)_2\text{-}M'$ or $M\text{-}(SO_2)_2\text{-}M'$ compounds. The additional sulfur dioxide is apparently involved in the formation of a polymeric product, as the solubility properties and the spectral characteristics attest (see Spectroscopic Section). The mode of attachment of this additional sulfur dioxide cannot be determined without structural analysis.

The insertion of sulfur dioxide into the metal-carbon bond in bis (cyclopentadienyl iron dicarbonyl)diphenyltin may not be merely a result of differing metal-carbon bond strengths in the phenylated and methylated tin compounds. The tin-carbon bonds in bis (cyclopentadienyl iron dicarbonyl)-diphenyltin may be further weakened by a change in the bonding orbitals of the tin atom. The tin-iron bond lengths in such compounds are often shorter than is the case in compounds with only one tin-iron bond. For example, the tin-iron bond length in triphenyltin(cyclopentadienyl)iron

dicarbonyl was found to be 2.53 angstroms (31). The tin-iron bond length in bis (cyclopentadienyl iron dicarbonyl)-dichlorotin was found to be 2.49 angstroms, and, in addition, the tin-chlorine bond lengths were longer than was the case in dimethyltin dichloride (60). This effect is clearly observed in the infrared spectra of this compound. The value of the tin-chlorine stretching frequency is indicative of a weakened tin-chlorine bond (61).

A similar effect may weaken the tin-carbon bond and strengthen the tin-iron bond in bis (cyclopentadienyl iron dicarbonyl)diphenyltin, resulting in insertion of sulfur dioxide into the tin-carbon rather than the tin-iron bond.

Sulfinates derived from tin (62), iron (57) and manganese (58) compounds contain one sulfur atom per metal atom. The organotin sulfinates tend to polymerize via intermolecular coordination. The spectroscopic properties of these compounds suggest that the tin atoms are pentacoordinate (62).

The tendency of metal-metal bonded compounds to incorporate more than one mole of sulfur dioxide per mole of compound may be due in part to the readiness of tin to adopt pentacoordination. Clearly, organotin sulfinates could also incorporate additional sulfur dioxide. The properties of the transition metal moiety which favor formation of products containing more than one mole of sulfur dioxide per mole of metal-metal bonded compound are not obvious. In the iron and manganese sulfinates, the transition metal

atom is apparently donating electron density to the sulfur atom (see Spectroscopic Section). Perhaps this effect is being transmitted to the tin atom, and the initial formation of a product containing one mole of sulfur dioxide per mole of metal-metal bonded compound is followed by intermolecular linkage by additional sulfur dioxide.

The compound trimethylgermanium(cyclopentadienyl)iron dicarbonyl also reacted with liquid sulfur dioxide, but a yellow, crystalline product identified as the 1:1 insertion product resulted.

$$(CH_3)_3GeFe(CO)_2(\pi\text{-}C_5H_5) + SO_2 \longrightarrow (CH_3)_3Ge\text{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}\text{-}Fe(CO)_2(\pi\text{-}C_5H_5)$$

Due to the smaller size of the germanium atom, the tendency toward pentacoordination is less for germanium than for tin. Thus the tendency for the sulfinates to polymerize by intermolecular coordination, or to incorporate additional sulfur dioxide would be less than for the corresponding tin compound. Hence the formation of this simple and crystalline 1:1 product, in contrast to the behavior of the tin-iron compound, is not surprising.

At room temperature, trimethylsilicon(cyclopentadienyl)-iron dicarbonyl did not react with liquid sulfur dioxide. Reaction took place at 80°, but the product could not be characterized. The bulk of the product was a black solid insoluble in common organic solvents. The remainder of the

material was a black tar of indefinite composition. It is unlikely that the difference in reactivity of the silicon-iron and germanium-iron bonds is due to steric considerations. It is possible that the unreactive nature of the silicon-iron bond is due to a slightly higher bond strength than is the case for the germanium-iron or tin-iron bonds. This is in agreement with the observed order of reactivity toward trifluoroiodomethane.

Similarly, in contrast to the ease of reaction of triphenyltinmangnese pentacarbonyl with sulfur dioxide (57), triphenylgermaniummanganese pentacarbonyl did not react with sulfur dioxide (53).

In insertion reactions as well as in cleavage reactions, metal-metal bonded compounds may undergo reaction at different sites. Both trimethyltin(cyclopentadienyl)iron dicarbonyl and the germanium analogue react with sulfur dioxide with cleavage of the metal-metal bond, but the products are dissimilar, possibly due to the more ready adoption of pentacoordination by the tin atom than by the germanium atom. The insertion of sulfur dioxide into the tin-carbon bonds in bis (cyclopentadienyl iron dicarbonyl)diphenyltin dramatically illustrates the importance of substituent effects.

CHAPTER IV

REACTIONS OF METAL-METAL BONDED COMPOUNDS WITH FLUORO-ALKYNES AND FLUORO-ALKENES

Introduction

The first report of a two carbon insertion into a metal-metal bond involved insertion of tetrafluoroethylene into hexamethylditin (16).

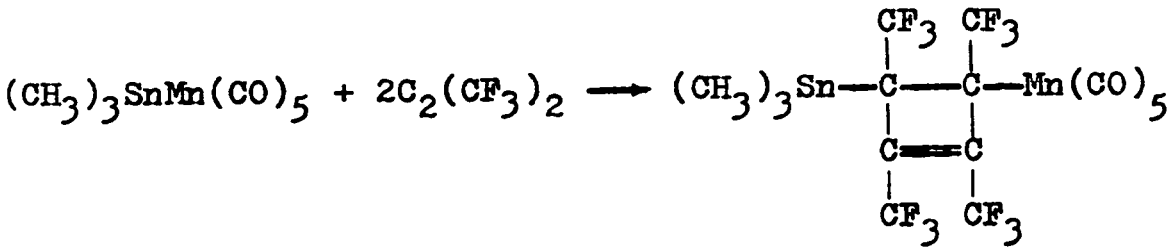
$$(CH_3)_6Sn_2 + C_2F_4 \longrightarrow (CH_3)_3Sn(C_2F_4)_nSn(CH_3)_3 + (CH_3)_3Sn(C_2F_4)_nH \qquad n = 1,2,3...$$

The formation of these products, and those arising from reaction with other fluoroethylenes, is best explained in terms of the intermediacy of radicals of the form $(CH_3)_3SnCF_2CXF\cdot$, (X = F,Cl,H). This mechanism is the same as that proposed for the reaction of hexafluorobut-2-yne with hexamethylditin (17).

The tin-manganese bond in trimethyltinmanganese pentacarbonyl undergoes insertion reactions with fluoro-olefins (9, 12). Insertion does not proceed without the assistance of ultraviolet light. Nevertheless, there is no evidence for the intermediacy of the trimethyltin radical, $(CH_3)_3Sn\cdot$.

No fluoroalkyl derivatives of tin, or products corresponding to the insertion of more than one mole of olefin into the tin-manganese bond, are found.

Hexafluorobut-2-yne also inserts into the tin-manganese bond (9). Further reaction may occur, forming cyclobutene derivatives, but no "growth reaction" products have been isolated.



Fluoro-olefins insert into the germanium-manganese bond in trimethylgermaniummanganese pentacarbonyl (13). As expected, elimination of gaseous trimethylfluorogermane from the insertion products is not as favored as the elimination of solid trimethyltin fluoride from the corresponding insertion products.

The reaction of an identical series of olefins with both trimethyltinmanganese pentacarbonyl and trimethylgermaniummanganese pentacarbonyl did not give rise to completely analogous products (12,13). The nature of the products favored an ionic or four-centered reaction mechanism, and it was suggested that the differences in the reaction products of the tin-manganese and germanium-manganese bonds might have been due to a difference in the polarity of the bonds.

A study of the effect of substitution on the tin atom in trimethyltinmanganese pentacarbonyl was not too revealing, however, since no derivative was found which would undergo the same variety of insertion reactions (9). Phosphine derivatives of trimethyltinmanganese pentacarbonyl are also considerably less reactive than the parent compound (63). Thus it is difficult to test the possibility that the polarities of the tin-manganese and germanium-manganese bonds differ.

It has been demonstrated that trimethyltinmanganese pentacarbonyl and trimethylgermaniummanganese pentacarbonyl undergo 1,4-addition to hexafluorobutadiene (64). The stereochemistry of the products favors an ionic rather than a concerted four-centered 1,4-addition.

The tin-cobalt bond reacts with tetrafluoroethylene to give a stable insertion product (11). In the reaction with trifluoroethylene, fragments are isolated which indicate that insertion occurred. A study of thermal insertion in a variety of solvents showed that the nature of the products depends on the polarity of the solvent. In highly polar solvents such as acetone and methanol, the reaction is that of the $Co(CO)_4^-$ anion. This accounts for the similarity in the products and the reaction rates of trimethyltincobalt tetracarbonyl and triphenyltincobalt tetracarbonyl (11).

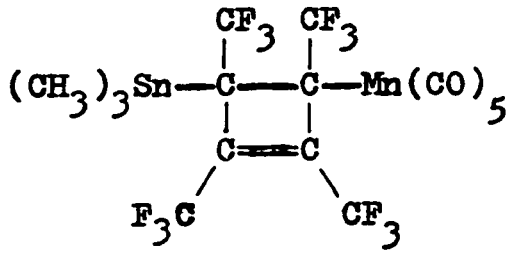
Clearly, further studies of metal-metal bonded compounds with fluoro-olefins are warranted, and useful information might be gained by examining the behavior of a related

sequence of compounds.

Results and Discussion

1) Hexafluorobut-2-yne with Metal-Metal Bonded Compounds

Hexafluorobut-2-yne reacts with trimethyltinmanganese pentacarbonyl to give products containing one or two butyne units (9). The product of empirical formula corresponding to $(CH_3)_3SnC_4(CF_3)_4Mn(CO)_5$ has been shown to be not a "growth reaction" product, but a cyclobutene derivative (65).



Recently, it has been shown that hexafluorobut-2-yne reacts with trimethylgermaniummanganese pentacarbonyl to form 1:1 and 2:1 insertion products (63). As was the case for the tin analogue, both products are formed during irradiation at room temperature or at 76°.

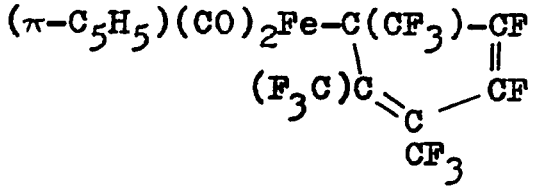
Under ultraviolet irradiation at room temperature, trimethyltin(cyclopentadienyl)iron dicarbonyl reacted with hexafluorobut-2-yne to give a product of empirical formula corresponding to $(CH_3)_3SnC_2(CF_3)_2Fe(CO)_2(\pi\text{-}C_5H_5)$. Spectroscopic information (see Chapter V) indicated that both the trimethyltin and cyclopentadienyl iron dicarbonyl moieties were still intact. Two carbonyl stretching frequencies

were observed in the infrared spectrum, suggesting that although carbon monoxide was evolved during the course of the reaction, there were still two carbonyl groups attached to the iron atom in the product. Integration of the proton n.m.r. spectrum of this compound gave the expected ratio of 9:5 for methyl and cyclopentadienyl resonances, respectively. In addition, the small coupling observed in the methyl resonance suggested that fluorine atoms were in close proximity to the tin atom (see Chapter V). The two resonances in the fluorine-19 n.m.r. spectrum indicated that the fluorine atoms were in only two different magnetic environments. This fact, coupled with the infrared stretching frequency observed at 1530 cm^{-1}, assignable to a C=C stretching mode, led to the conclusion that this compound was a result of insertion of hexafluorobut-2-yne into the tin-iron bond.

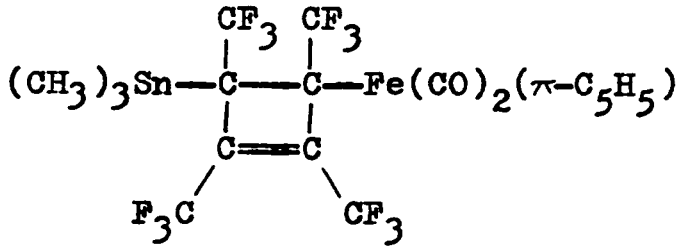
In view of the ready formation of a 2:1 insertion product with trimethyltinmanganese pentacarbonyl, the reaction of trimethyltin(cyclopentadienyl)iron dicarbonyl with hexafluorobut-2-yne was studied under more vigorous conditions. Following ultraviolet irradiation at 76°, two new products were isolated, neither of which was a cyclobutene derivative.

The major product, of empirical formula corresponding to $(\pi\text{-}C_5H_5)(CO)_2FeC_8F_{11}$, was apparently the product of elimination of trimethyltin fluoride from the expected cyclobutene derivative. On the basis of spectroscopic considerations discussed in Chapter V, this compound was

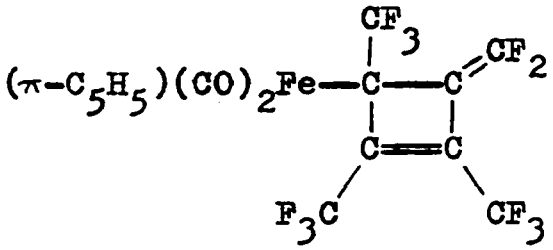
assigned the structure



Its formation can thus be explained in terms of trimethyltin fluoride elimination from



to give an exocyclic product.



This would readily rearrange to the final product containing the cyclopentadiene ring.

The minor product, of empirical formula corresponding to $(\pi\text{-}C_5H_5)(CO)_2FeC_4F_6H$, was apparently formed by elimination of the trimethyltin radical from the 1:1 insertion product, followed by abstraction of a hydrogen atom by the resulting radical. On the basis of spectroscopic considerations discussed in Chapter V, this product was assigned the structure <u>trans</u>-$H(CF_3)C{=}C(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$.

Both trimethylsilicon(cyclopentadienyl)iron dicarbonyl and the germanium analogue gave only 1:1 insertion products when irradiated at room temperature with hexafluorobut-2-yne. Irradiation at 76° did not give rise to cyclobutene derivatives, or to other products which might indicate that a cyclobutene derivative had been formed. Similarly, irradiation of the 1:1 product from insertion into the germanium-iron bond at 76° with excess hexafluorobut-2-yne did not result in the formation of any cyclobutene product or derivatives thereof.

2) 3,3,3-Trifluoropropyne with Metal-Metal Bonded Compounds

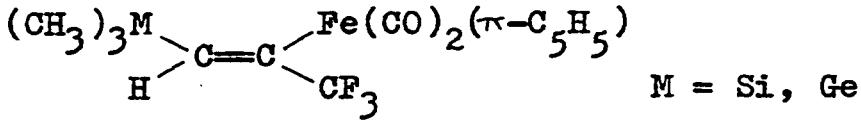
The ready insertion of hexafluorobut-2-yne into the silicon-iron, germanium-iron, and tin-iron bonds indicated that other alkynes might react similarly. An unsymmetrical alkyne, 3,3,3-trifluoropropyne was chosen, not only because of its availability, but also because it was expected that the hydrogen atom in this alkyne would prove to be very valuable for the spectroscopic determination of the isomeric composition of the products. In addition, it should be possible to observe ^{119}Sn-C-H coupling in the proton n.m.r. signal of this hydrogen atom if both it and the tin atom were attached to the same carbon atom in an insertion product. Thus a series of 3,3,3-trifluoropropyne insertion products would provide valuable information about the nature of the mechanism of these insertion reactions.

Reaction of trimethyltin(cyclopentadienyl)iron dicarbonyl

gave a low yield of cis-$H(CF_3)C{=}C(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$ and a corresponding amount of trimethyltin fluoride. The remainder of the metal-metal bonded compound was not recovered. It is interesting that this product is the same as that obtained from the reaction of cyclopentadienyl iron dicarbonyl anion and 3,3,3-trifluoropropyne (14).

Under thermal conditions in hexane at 80°, trimethyltin-(cyclopentadienyl)iron dicarbonyl did not react with 3,3,3-trifluoropropyne. Both materials were recovered unchanged.

Both trimethylsilicon(cyclopentadienyl)iron dicarbonyl and its germanium analogue reacted with 3,3,3-trifluoropropyne to give products of empirical formula corresponding to $(CH_3)_3MC_2H(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$, where M = Si, Ge. On the basis of the spectroscopic evidence discussed in Chapter V, these are tentatively assigned the structures



M = Si, Ge

These are the first examples of insertion of an unsymmetrical acetylene into a metal-metal bond.

A very minor product in the reaction of trimethylsilicon-(cyclopentadienyl)iron dicarbonyl with 3,3,3-trifluoropropyne was spectrally similar to the cyclobutene derivatives discussed earlier. Unfortunately, there was insufficient material for any spectrum other than an infared spectrum.

The role of the ultraviolet irradiation in these

reactions is not known. The formation of cis-isomeric products favors a four-centered rather than a radical mechanism.

Similarly, the formation of cyclobutene derivatives in these insertion reactions rather than "growth reaction" products is indicative of a four-centered rather than a radical mechanism.

3) Perfluorocyclobutene with Metal-Metal Bonded Compounds

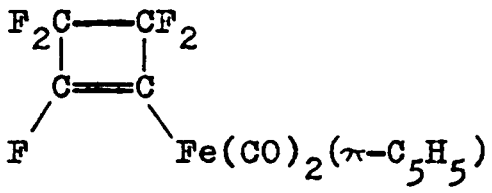
Both the germanium-manganese bond and the tin-manganese bond react with tetrafluoroethylene, trifluoroethylene, and chlorotrifluoroethylene (9,12,13). Only the tetrafluoroethylene insertion product is stable. In general, trimethyltin fluoride or trimethylfluorogermane is eliminated and fluorovinyl derivatives of manganese pentacarbonyl are isolated.

The ready insertion of fluorinated acetylenes into bonds between iron and the Group IVA metals indicated that insertion of fluorinated ethylenes might also be possible. The expected elimination products should be stable, in view of the stability of the fluorovinyl derivatives of iron synthesized by Stone and co-workers (14,15,63).

However, in contrast to the ready insertion of perfluorocyclobutene into the tin-manganese bond (9), there was no reaction between perfluorocyclobutene and trimethyltin(cyclopentadienyl)iron dicarbonyl. Although trimethyltin fluoride was isolated, no fluorovinyl derivatives of

iron were detected. Cyclopentadienyl iron dicarbonyl dimer was formed. Apparently the metal-metal bonded compound is not sufficiently stable to ultraviolet irradiation for reaction to take place. This difficulty has also been encountered in the corresponding reactions of trimethyltin-(cyclopentadienyl)molybdenum tricarbonyl and its tungsten analogue (22).

Neither the silicon-iron nor the germanium-iron bond reacted with perfluorocyclobutene. Although trimethyl-fluorosilane (or germane) were isolated, no fluorovinyl compound of iron was detected, even though the expected elimination product,



is known (66).

4) <u>Trifluoroethylene with Metal-Metal Bonded Compounds</u>

The ultraviolet assisted reaction of trimethylsilicon-(cyclopentadienyl)iron dicarbonyl with trifluoroethylene produced cyclopentadienyl iron dicarbonyl dimer and trimethylfluorosilane. A small amount of what was apparently a mixture of iron fluorovinyls was isolated. The low yield did not permit full characterization.

The reactions of trimethylgermanium(cyclopentadienyl)-iron dicarbonyl and its tin analogue with trifluoroethylene

were similar to that of the silicon-iron compound.

In view of the reaction of trimethyltincobalt tetracarbonyl with trifluoroethylene in acetone, which is considered a reaction of the tetracarbonylcobaltate(1) anion (11), the reaction of trimethyltin(cyclopentadienyl)iron dicarbonyl with trifluoroethylene was studied in acetone under thermal conditions. However, the metal-metal bonded compound disproportionated into tetramethyltin and bis (cyclopentadienyl iron dicarbonyl)diphenyltin without reaction with trifluoroethylene. Thus it is unlikely that a dissociative mechanism is operative in the reactions of metal-metal bonded compounds containing iron.

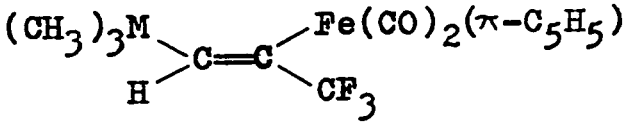
5) Chlorotrifluoroethylene with Metal-Metal Bonded Compounds

The reactions of trimethylsilicon(cyclopentadienyl)-iron dicarbonyl and its germanium analogue gave cyclopentadienyl iron dicarbonyl dimer and a mixture of trimethylchlorosilane (or germane) and trimethylfluorosilane (or germane). No fluorovinyls of iron were isolated.

The reaction of trimethyltin(cyclopentadienyl)iron dicarbonyl with chlorotrifluoroethylene gave cyclopentadienyl iron dicarbonyl dimer, trimethyltin chloride, and a trace of trimethyltin fluoride. Although some fluorovinyl compound of iron was produced, the amount was insufficient to permit full characterization.

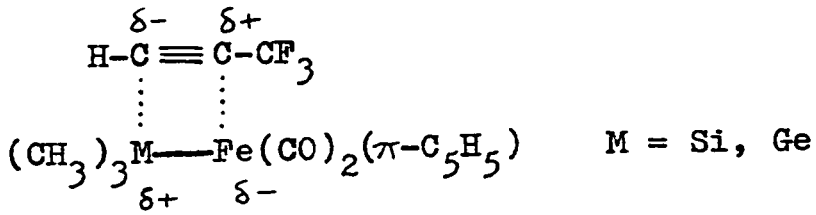
Conclusions

Hexafluorobut-2-yne is readily inserted into the silicon-, germanium-, and tin-iron bonds. 3,3,3-Trifluoropropyne reacted with the silicon- and germanium-iron bonds. Although the insertions were ultraviolet assisted, no products suggestive of a radical mechanism (15) were found. These insertions likely proceed via a four-centered or ionic mechanism. In the reaction of 3,3,3-trifluoropropyne with the silicon- and germanium-iron bonds, the product likely has the configuration



M = Si,Ge

The charge separation in the transition state involved in the formation of these compounds is consistent with that observed in the cleavage reaction of the metal-metal bonds.



M = Si, Ge

The failure of the three metal-metal bonded compounds to react with fluorinated ethylenes may be due to their inherent instability toward ultraviolet irradiation. Many of the expected elimination products are known compounds, but are not detected in these reactions. Instead, cyclopentadienyl iron dicarbonyl dimer was isolated in good yield.

CHAPTER V

SPECTROSCOPIC STUDIES

A: Metal-Metal Bonded Compounds

There have been many studies of the change in position of the carbonyl stretching mode in metal carbonyl compounds with changes in ligands on the metal (67,68,69,70). For the cyclopentadienyl iron dicarbonyl moiety, it is not possible to estimate the σ-donor and π-acceptor effects of ligands from the change in the carbonyl stretching mode since there is no carbonyl trans to any ligand.

The frequencies of the principal infrared absorptions of trimethyltin(cyclopentadienyl)iron dicarbonyl and chlorodimethyltin(cyclopentadienyl)iron dicarbonyl are shown in Table IV. The frequencies of the principal infrared absorptions of trimethylsilicon(cyclopentadienyl)iron dicarbonyl and trimethylgermanium(cyclopentadienyl)iron dicarbonyl are shown in Table V. The accuracy of the carbonyl stretching absorptions is $\pm\frac{1}{2}$ cm^{-1} (recorded in cyclohexane solution). The accuracy of the other absorptions is ± 5 cm^{-1}.

Clearly the value of the carbonyl stretching absorptions

TABLE IV

INFRARED SPECTRA OF SOME METAL-METAL BONDED COMPOUNDS

Assignment	$(CH_3)_3SnFe(CO)_2Cp$ [a]	$Cl(CH_3)_2SnFe(CO)_2Cp$
C-H asym str Cp	3120 vw	3110 w
C-H asym str CH_3	2990 w	2890 w
C-H sym str CH_3	2920 w	2910 w
C=O str	1991 vs	1999 vs
	1942 vs	1959 vs
H def Cp	1435 vw	1425 w
	1415 w	1410 w
	1180 w	1175 vw
	1005 w	1010 w
	995 w	1000 w
Cp ring breathe	840 m	840 m
Sn-CH_3 rock	755 s	770 m
	690 w	740 m
	635 s	630 s
Fe-CO def	580 vs	580 vs
Sn-C asym str	510 s	510 m,sh
Sn-C sym str	495 s	505 s
Fe-C str	460 vw	450 vw

a Cp = (π-C_5H_5)

s = strong; m = medium; w = weak; v = very; sh = shoulder

TABLE V

INFRARED SPECTRA OF SOME METAL-METAL BONDED COMPOUNDS

Assignment	$(CH_3)_3GeFe(CO)_2Cp$ [a]	$(CH_3)_3SiFe(CO)_2Cp$
C-H asym str Cp	3130 vw	3120 vw
C-H asym str CH_3	2980 m	2950 m
C-H sym str CH_3	2910 m	2890 m
C=O str	1997 vs	1998 vs
	1945 vs	1944 vs
H def Cp	1430 w	1430 w
H asym def CH_3	1415 m	1415 m
H sym def CH_3	1220 m	1240 s
	1015 w	1010 w
	995 w	995 w
Cp ring breathe	840 m,sh	
Si-CH_3 rock		820 vs
Ge-CH_3 rock	810 s	
	740 m	740 s
Si-C asym str		670 m
	640 s	640 s
Si-C sym str		610 m
Fe-CO def	590 vs	590 vs
Ge-C asym str	580 s,sh	
Ge-C sym str	550 s	
	515 m	515 m
Fe-C str	440 w	440 w

a Cp = (π-C_5H_5)

s = strong; m = medium; w = weak; v = very; sh = shoulder

is lowest in trimethyltin(cyclopentadienyl)iron dicarbonyl. However, there is no clear separation between the carbonyl stretching frequencies of the silicon and germanium compounds (Table V). The trend in carbonyl stretching frequencies follows the expected order if the increase is due to the inductive effect of the Group IV atom (67).

Similarly, the increase in the carbonyl stretching frequency in chlorodimethyltin(cyclopentadienyl)iron dicarbonyl over that for the trimethyltin compound (Table IV) may be attributed to the inductive effect of the chlorine atom (71).

The n.m.r. spectra of the metal-metal bonded compounds show essentially the same trends (see Table VI). Both the methyl and cyclopentadienyl resonances are shifted to lower field in chlorodimethyltin(cyclopentadienyl)iron dicarbonyl as expected from the introduction of the electronegative chlorine atom (40).

It is interesting therefore that the spectroscopic results suggest only small differences between the silicon-iron, germanium-iron, and tin-iron bonds, even though, as shown in previous chapters, there are substantial differences in their chemical reactivity.

B: Compounds of Sulfur Dioxide

Wojcicki has demonstrated that the infared spectra of metal S-sulfinates exhibit two intense absorptions in the 1035-1205 cm^{-1} region, about 100-200 cm^{-1} lower than the

TABLE VI

PROTON N.M.R. DATA FOR SOME METAL-METAL BONDED COMPOUNDS

Compound	τ^* ($M-CH_3$)	$J_{^{119}Sn-C-H}$	τ^* (C_5H_5)
$(CH_3)_3SnFe(CO)_2(\pi-C_5H_5)$	9.7 M = Sn	47 c.p.s.	5.3
$Cl(CH_3)_2SnFe(CO)_2(\pi-C_5H_5)$	9.2 M = Sn	40 c.p.s.	5.1
$(CH_3)_3GeFe(CO)_2(\pi-C_5H_5)$	9.6 M = Ge		5.3
$(CH_3)_3SiFe(CO)_2(\pi-C_5H_5)$	9.6 M = Si		5.3

* in chloroform

TABLE VII

PROTON N.M.R. DATA FOR SOME COMPOUNDS OF SULFUR DIOXIDE

Compound	τ^* ($M-CH_3$)	τ^* (C_5H_5)
$(CH_3)_3SnFe(CO)_2(\pi-C_5H_5)\cdot 1.5SO_2$	9.3 M = Sn	5.0
$(CH_3)_3GeSO_2Fe(CO)_2(\pi-C_5H_5)$	9.5 M = Ge	5.0

* in chloroform

corresponding bands in organic sulfones (52,53). This displacement is attributed to π-interaction between the iron and sulfur atoms.

The symmetric and asymmetric SO-stretching frequencies are at 1075 and 1205 cm^{-1}, respectively, in the product of insertion into trimethylgermanium(cyclopentadienyl)iron dicarbonyl (Table VIII), indicating that this product is an S-sulfinate, with both the iron atom and the germanium atom bound to sulfur. The observed frequencies are slightly higher than those for the series of compounds prepared by Bibler and Wojcicki (52). However, the stretching frequencies in a series of compounds $(\pi\text{-}C_5H_5)(CO)_2Fe(SO_2R)$ were found to be quite insensitive to the nature of the group "R". Large changes in stretching frequencies are only observed for complexes bearing a charge (53,72,73).

The insertion of sulfur dioxide into trimethyltin-(cyclopentadienyl)iron dicarbonyl produces a different type of product. The SO-stretching frequencies are at 950-990 cm^{-1}, although weaker, broad absorptions occur in the region of 1150 cm^{-1} (see Table VIII). The tin-methyl stretching mode is no longer observed at approximately 500 cm^{-1}, although it probably constitutes a part of the intense absorption at 540 cm^{-1}. Similarly, the ^{119}Sn-C-H coupling constant increases from 48 c.p.s. in trimethyltin(cyclopentadienyl)iron dicarbonyl to 64 c.p.s. in the insertion product (see Table VII). These SO-stretching frequencies and the change in coupling constants are similar to those observed in the

TABLE VIII

INFRARED SPECTRA OF SOME COMPOUNDS OF SULFUR DIOXIDE

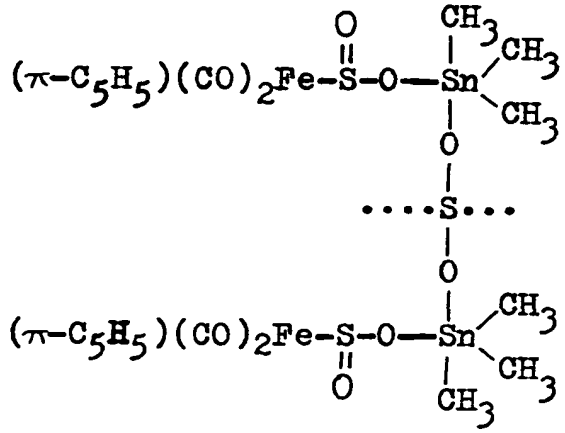
Assignment	$(CH_3)_3GeSO_2Fe(CO)_2Cp$*	$(CH_3)_3SnFe(CO)_2Cp \cdot 1.5SO_2$
C-H asym str Cp	3120 w	3110 vw
C-H asym str CH_3	2990 w	2960 vw
C-H sym str CH_3	2920 w	2900 vw
C=O str	2060 vs	2050 vs
	2000 vs	2000 vs
H def Cp	1430 w	1425 w
H asym def CH_3	1420 w	
		1220 m
S=O asym str	1205 vs	
		1150 m,sh
		1100 s
S=O sym str	1075 vs	
		990 vs,broad
ring breathe	850 m	840 m
Ge-CH_3 rock	790 vs	
Sn-CH_3 rock		780 vs
	650 m	640 m
	620 vs	615 vs
		600 vs
Ge-C asym str	585 m	
Fe-CO def	570 vs	565 vs
Sn-C str		550 vs
Ge-C sym str	540 m	
	500 w	490 w
Fe-C str	440 vw	440 w

* Cp = (π-C_5H_5)

s = strong; m = medium; w = weak; v = very; sh = shoulder

compound $(CH_3)_3SnMn(CO)_5 \cdot 1.5SO_2$ (57), and in the general compound $(CH_3)_3Sn(SO_2R)$ (62). The lowering of the SO-stretching frequencies is attributed to intermolecular bonding. The infrared and n.m.r. data indicate the presence of an approximately planar trimethyltin group (62).

Unlike the reaction of bis (cyclopentadienyl iron dicarbonyl)diphenyltin, metal-metal bond cleavage is indicated. The infrared spectra is consistent with the presence of Sn-O-S(O)-Fe units, but the mode of attachment of the additional sulfur dioxide is unknown. If the rather naive assumption is made that the additional sulfur dioxide merely links two tin atoms, the structure could be



Polymerization could also occur by intermolecular coordination of oxygen atoms to the extra sulfur atom.

C: Compounds with Hexafluorobut-2-yne

1) Products from Insertion into Metal-Metal Bonds

The positions of the principal infrared absorptions of the products from the insertion of hexafluorobut-2-yne into the metal-metal bonds are shown in Tables IX and X.

The infrared spectra of the three butyne insertion products are very similar. Characteristic bands occur at 1530 cm^{-1} (C=C stretching mode) and at 1240, 1210, 1160, 1120, and 1100 cm^{-1} (C-F stretching modes). These bands are also observed in the infrared spectrum of the analogous derivative of trimethyltinmanganese pentacarbonyl (9).

The chemical shifts of the resonances observed in the n.m.r. spectra of the three insertion products are given in Table XI. The methyl resonances contain a small coupling (approximately 1 c.p.s.) which gives rise to peaks which are apparently quartets. Unfortunately, the fluorine-19 resonances (Table XII) are too broad in all cases to determine which of the two observed resonances contain this one cycle coupling.

If the insertion products are cis-butene derivatives, the fluorine-19 resonances of the two trifluoromethyl groups should be coupled by about 10 c.p.s., whereasthe coupling in the trans-butene derivative should be on the order of 1 c.p.s. (74). Unfortunately, the observed resonances are over 10 c.p.s. wide, and no determination of isomeric composition is possible.

TABLE IX

INFRARED SPECTRA OF SOME COMPOUNDS OF HEXAFLUOROBUT-2-YNE

Assignment	Compound I	Compound II	Compound III
C-H asym str C_5H_5	3140 vw	3150 vw	3140 vw
C-H asym str CH_3	2980 w		
C-H sym str CH_3	2920 w		
C=O str	2020 vs	2040 vs	2040 vs
	1975 vs	1990 vs	1990 vs
	1940 m,sh	1960 m,sh	
C=C str			1780 s
C=C str	1535 w	1610 m	1650 m
	1435 vw	1435 vw	1435 vw
			1355 m
C-F str	1240 m	1290 s	1285 vs
	1210 vs	1220 vs	1250 vs
	1160 m		1210 vs
	1120 vs	1120 vs	1140 vs
	1100 vs		
			1040 m
	1010 vw	1015 vw	1015 vw
	850 m	850 m	
C_5H_5 ring breathe	840 m	840 m	840 m
	770 m		
		650 s	700 m
	640 m	640 m	630 m
Fe-CO def	575 m	575 m	575 m
	550 m	545 m	545 m
Sn-C asym str	530 w		
Sn-C sym str	510 w		

Compound I = $(CH_3)_3SnC_4F_6Fe(CO)_2(\pi\text{-}C_5H_5)$

Compound II = $(\pi\text{-}C_5H_5)(CO)_2FeC_4F_6H$

Compound III = $(\pi\text{-}C_5H_5)(CO)_2FeC_8F_{11}$

s = strong; m = medium; w = weak; v = very; sh = shoulder

TABLE X

INFRARED SPECTRA OF SOME COMPOUNDS OF HEXAFLUOROBUT-2-YNE

Assignment	$(CH_3)_3GeC_4F_6Fe(CO)_2Cp$*	$(CH_3)_3SiC_4F_6Fe(CO)_2Cp$
C-H asym str Cp	3150 vw	3150 vw
C-H asym str CH_3	2970 w	2960 m
C-H sym str CH_3	2900 w	2900 m
C=O str	2030 vs	2030 vs
	1990 vs	1990 vs
	1960 m,sh	1960 m,sh
C=C str	1530 w	1515 w
C-H asym def CH_3		1250 m
	1240 w	
C-F str	1210 vs	1210 vs
	1165 w	1160 m
	1130 vs	1130 vs
	1100 vs	1105 vs
	1000 vw	1000 vw
Cp ring breathe	845 m	
		840 s
Ge-CH_3 rock	830 m,sh	
Si-C asym str		670 w
	645 m	645 m
Si-C sym str		620 w
Ge-C asym str	600 w	
Fe-CO def	575 m	575 m
Ge-C sym str	565 w,sh	
	550 m	550 m

* Cp = (π-C_5H_5)

s = strong; m = medium; w = weak; v = very; sh = shoulder

TABLE XI

PROTON N.M.R. DATA FOR SOME COMPOUNDS OF HEXAFLUOROBUT-2-YNE

Compound	τ^* ($M-CH_3$)	τ (C_5H_5)	τ
$(CH_3)_3SnC_4F_6Fe(CO)_2(\pi-C_5H_5)$	9.8 M = Sn	5.1	
$(CH_3)_3GeC_4F_6Fe(CO)_2(\pi-C_5H_5)$	9.6 M = Ge	5.1	
$(CH_3)_3SiC_4F_6Fe(CO)_2(\pi-C_5H_5)$	9.8 M = Si	5.1	
$(\pi-C_5H_5)(CO)_2FeC_4F_6H$		5.1	3.4 multiplet
$(\pi-C_5H_5)(CO)_2FeC_8F_{11}$		5.2	

* in chloroform

TABLE XII

FLUORINE-19 N.M.R. DATA FOR SOME HEXAFLUOROBUT-2-YNE COMPOUNDS

Compound	δ^* (p.p.m.)	
$(CH_3)_3SnC_4F_6Fe(CO)_2(\pi-C_5H_5)$	49.4	50.4
$(CH_3)_3GeC_4F_6Fe(CO)_2(\pi-C_5H_5)$	50.0	50.5
$(CH_3)_3SiC_4F_6Fe(CO)_2(\pi-C_5H_5)$	50.0	51.7
$(\pi-C_5H_5)(CO)_2FeC_4F_6H$	58.0 multiplet	60.4 multiplet

* in $CFCl_3$ for which $\delta = 0$

The low field resonance in the fluorine-19 spectra of the product from insertion into the tin-iron bond has two small satellites. These could be the $^{119}Sn-CF_3$ couplings (J=24 c.p.s.). If this is the case, then the lower peak corresponds to the trifluoromethyl group closest to the tin atom.

The lack of fine structure in the fluorine-19 spectra of the three insertion products precludes proper assignment.

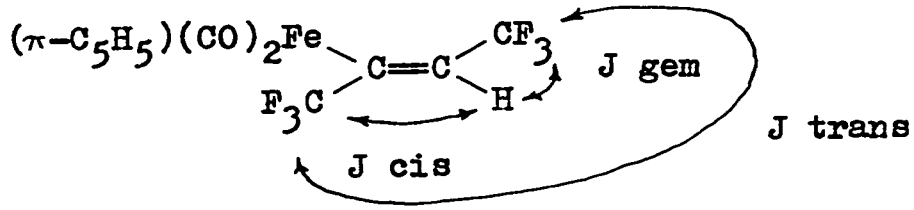
2) Fluorocarbon Derivatives of Cyclopentadienyl Iron Dicarbonyl

The positions of the principal infrared absorptions of the fluorocarbon derivatives of cyclopentadienyl iron dicarbonyl are shown in Table IX.

The infrared spectrum of the compound $(\pi-C_5H_5)(CO)_2FeC(CF_3)=C(CF_3)H$ is similar to those of the butyne insertion products. Again, the characteristic absorptions are at 1610 cm^{-1} (C=C stretching mode) and at 1240, 1220, and 1120 cm^{-1} (C-F stretching mode), in addition to the expected carbonyl and cyclopentadienyl peaks.

The n.m.r. spectrum of this compound (Table XI) consists of a singlet (cyclopentadienyl resonance) and a quartet of quartets (J_1 = 8.5 c.p.s., J_2 = 1.5 c.p.s.). The fluorine-19 spectrum (Table XII) consists of a pair of quartets and an overlapping pair of quartets. The pair of quartets at 58.0 p.p.m. upfield from freon-11 are separated by 8.0 c.p.s. and have an internal coupling of 2.0 c.p.s. The overlapping

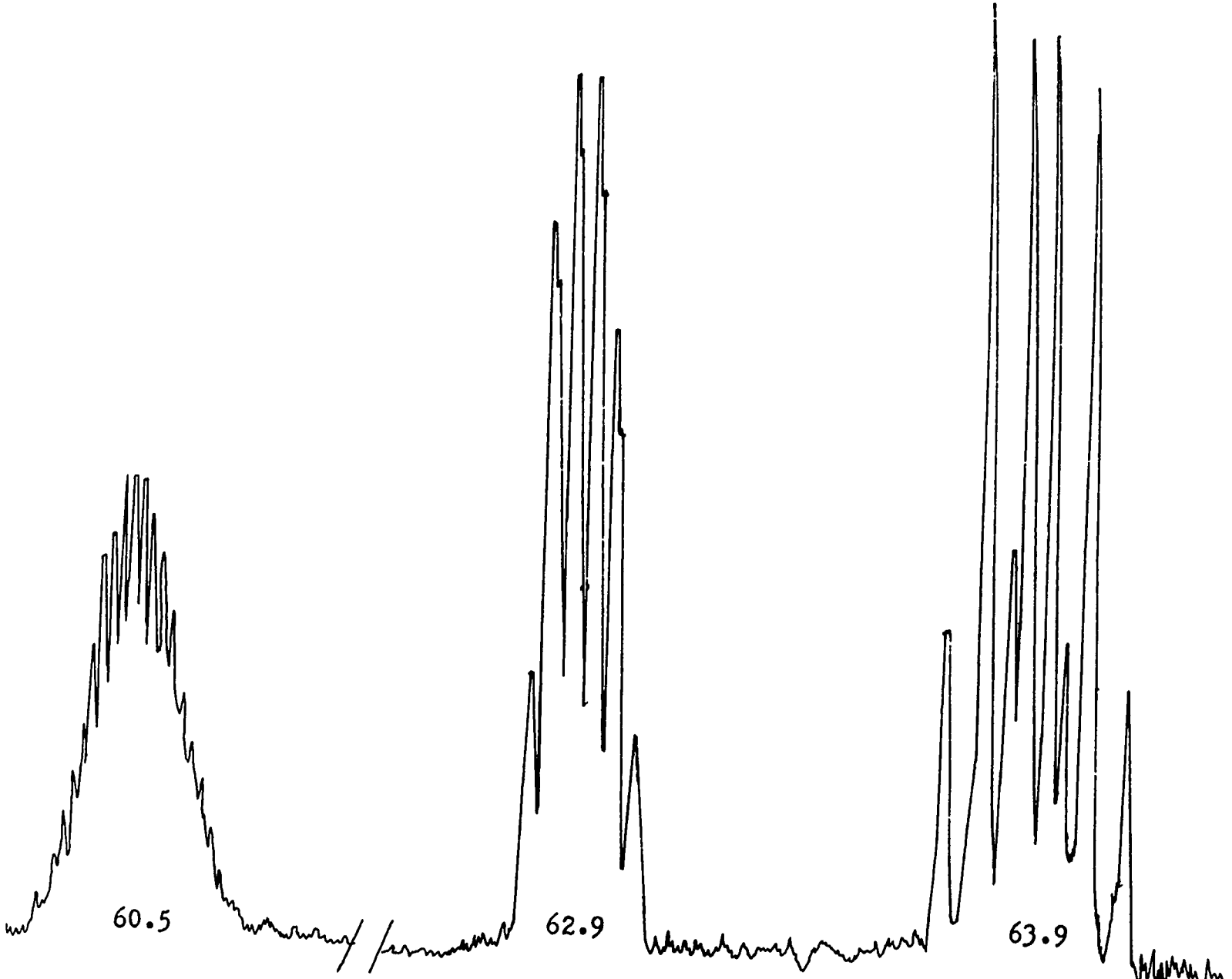
pair of quartets at 60.4 p.p.m. have a separation of approximately 2 c.p.s. and an internal coupling of approximately 2 c.p.s. (within the limits of measurement). Thus all the n.m.r. data is consistent with a <u>trans</u>-butene structure, with geminal CF_3-H coupling of 8.5 c.p.s., <u>cis</u> CF_3-H coupling of 1.5 c.p.s., and <u>trans</u> CF_3-CF_3 coupling of 2 c.p.s.



In the <u>cis</u>-butene derivative, the <u>trans</u> CF_3-H coupling would be expected to be close to zero (75).

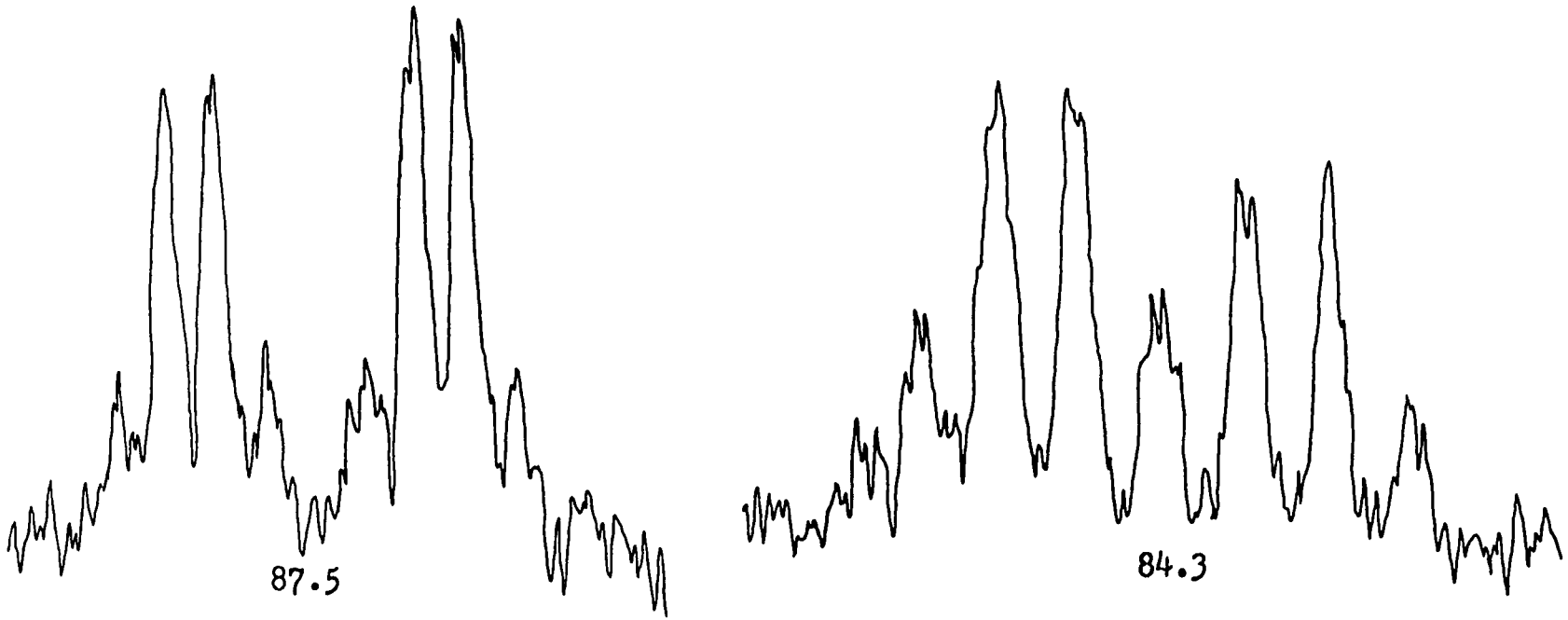
The infrared spectrum of the second fluorocarbon derivative of cyclopentadienyl iron dicarbonyl is much more complex (see Table IX). The two intense bands at 1650 and 1780 cm^{-1} are indicative of conjugated carbon-carbon double bonds (76,77,78). The carbon-fluorine stretching region is very complex, due to the presence of both =C-F and CF_3 groups.

The chemical shifts of the observed resonances in the proton n.m.r. spectrum of this cyclopentadiene derivative are given in Table XI. As is depicted in Figure I, five well-separated multiplets are observed in the fluorine-19 n.m.r. spectrum. On the basis of those observed in similar compounds (74,79,80), the following couplings may be expected in a compound with the suggested structure



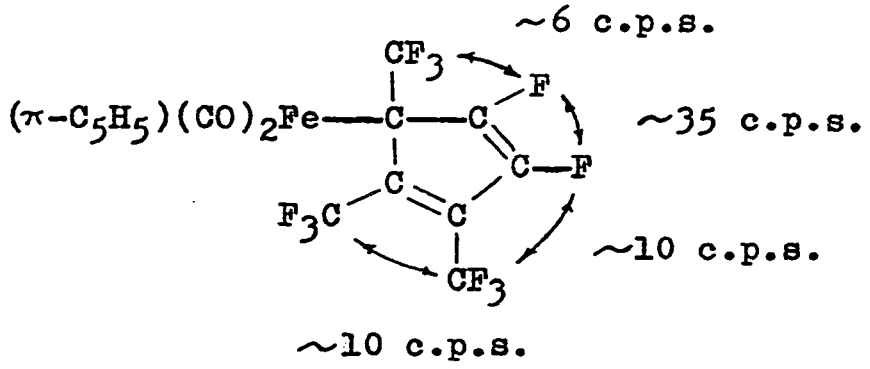
FLUORINE-19 N.M.R. SPECTRUM OF $(\pi\text{-}C_5H_5)(CO)_2FeC_8F_{11}$

FIGURE IA

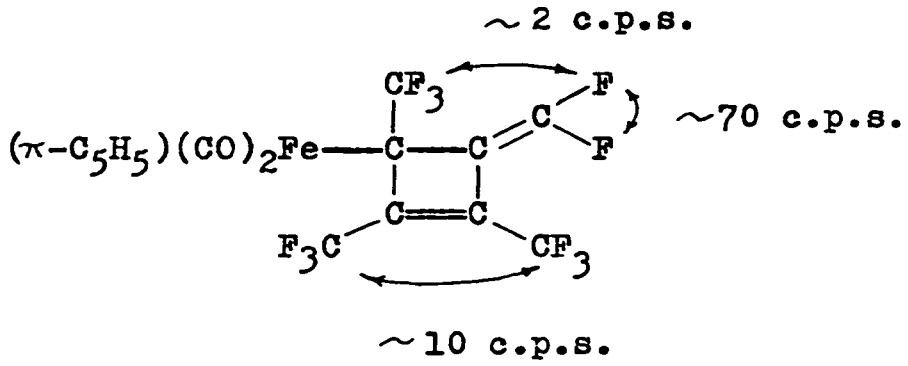


FLUORINE-19 N.M.R. SPECTRUM OF $(\pi\text{-}C_5H_5)(CO)_2FeC_8F_{11}$

FIGURE IB



whereas if the compound is the expected product from elimination of trimethyltin fluoride from a cyclobutene derivative, the following couplings would be expected:

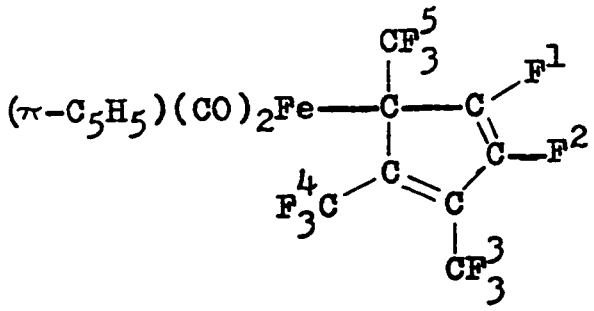


The separation between the two quartets in each multiplet assigned to the single fluorines on the ring is clearly 33.5 c.p.s. On the basis of this spectroscopic evidence, this compound is likely a cyclopentadiene derivative, although other supporting evidence would be desirable.

The resonances at 60.5, 62.9, and 63.9 p.p.m. upfield from freon-11 (ratio 1:1:1) are attributed to the three trifluoromethyl groups in the proposed structure. The resonance at lowest field is a very complex multiplet. The multiplet at 62.9 p.p.m. is an overlapping pair of quartets,

with a separation between the quartets of 7 c.p.s. and a coupling of 3.5 c.p.s. within the quartet. The multiplet at 63.9 p.p.m. is a doublet (J = 9.4 c.p.s.), each line of which is split into a quartet (J = 5.7 c.p.s.).

The assignment of these resonances to the proposed structure is as follows:



The multiplet at 87.5 p.p.m., assigned to F^1, is split into a doublet by coupling to F^2 (J = 33.5 c.p.s.), and split further into a pair of quartets by coupling with F^5 (J = 7 c.p.s.). In addition,there appears to be a small coupling with F^3 (J = 1.5 c.p.s.), to further split the lines in the observed pair of quartets.

The multiplet at 84.3 p.p.m. is assigned to F^2, which is coupled to F^1 (J = 33.5 c.p.s.) and to F^3 (J = 9.4 c.p.s.), resulting in a pair of quartets. The lines in the multiplet are further split, presumably by coupling with F^4 ($J \sim 2$ c.p.s.).

The multiplet at 63.9 p.p.m., assigned to F^3, is split into a doublet by coupling with F^2 (J = 9.4 c.p.s.) and split further into overlapping quartets by coupling with F^4 (J = 5.7 c.p.s.).

The multiplet at 62.9 p.p.m. is assigned to F^5, which

is coupled to F^1 (J = 7 c.p.s.) and to F^4 (J = 3.2 c.p.s.), resulting in an overlapping pair of quartets.

The complex multiplet remaining (at 60.5 p.p.m.) is then assigned to F^4 by elimination.

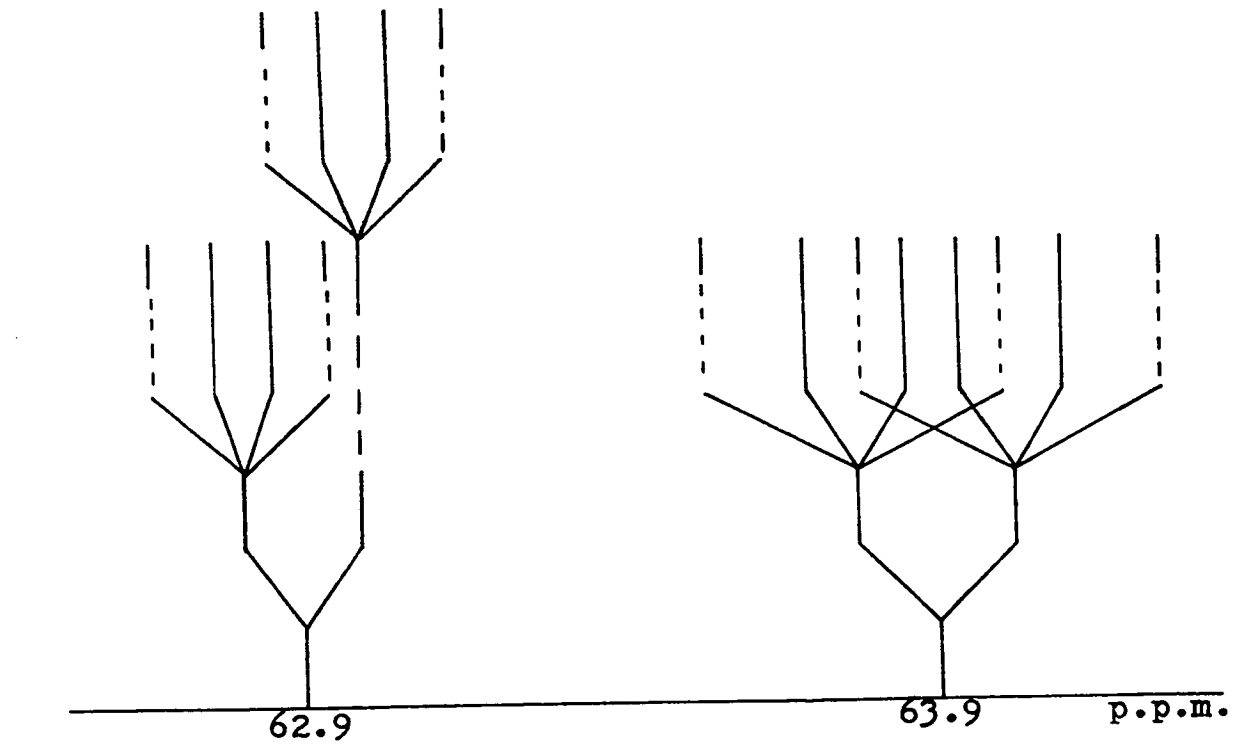
The detailed analysis of the fluorine-19 spectrum of this compound is shown in Figure II.

D: Compounds with 3,3,3-Trifluoropropyne

The infrared and n.m.r. spectra of the known compound $(\pi\text{-}C_5H_5)(CO)_2FeC(H)=C(CF_3)H$ (14) will not be discussed here.

The positions of the bands in the infrared spectra of the products from insertion of 3,3,3-trifluoropropyne into the silicon-iron and germanium-iron bonds are shown in Table XIII. Characteristic features are the peak at 1550 cm^{-1} (C=C stretching mode) and those at 1210, 1125, and 1090 cm^{-1} (C-F stretching modes).

The chemical shifts of the peaks in the proton n.m.r. spectra of the insertion products are given in Table XIV. Both the methyl and cyclopentadienyl resonances are sharp singlets. The quartet at lower field (J = 2 c.p.s.) indicates that the hydrogen atom from the 3,3,3-trifluoropropyne is cis to the trifluoromethyl group in the insertion product, since the coupling between the hydrogen atom and the trifluoromethyl group would be expected to be zero in the trans isomer (75). This 2 c.p.s. coupling is observed in the fluorine-19 n.m.r. spectra of the insertion products



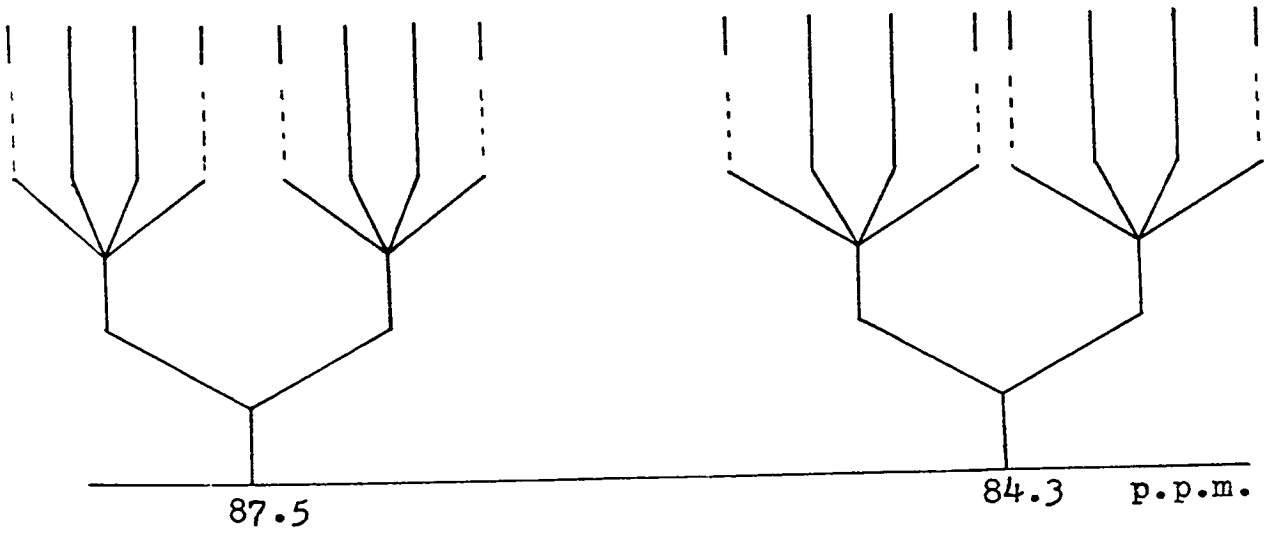


FIG. II ^{19}F N.M.R. SPECTRUM OF $(\pi\text{-}C_5H_5)(CO)_2FeC_8F_{11}$ (DETAIL)

TABLE XIII

INFRARED SPECTRA OF SOME COMPOUNDS OF 3,3,3-TRIFLUOROPROPYNE

Assignment	$(CH_3)_3GeCHCF_3Fe(CO)_2Cp$*	$(CH_3)_3SiCHCF_3Fe(CO)_2Cp$
C-H asym str Cp	3130 vw	3130 vw
C-H asym str CH_3	2970 w	2980 m
C-H sym str CH_3	2910 w	2900 w
C=O str	2020 vs	2020 vs
	1980 vs	1980 vs
C=C str	1555 m	1550 m
C-H asym def CH_3	1425 w	1425 w
	1280 w	1290 w
C-H sym def CH_3	1235 m	1250 s
C-F str	1205 vs	1210 vs
	1125 vs	1125 vs
	1090 vs	1090 vs
	860 s,sh	870 m,sh
Si-CH_3 rock		840 vs
Ge-CH_3 rock	825 vs	
Si-C asym str		665 m
	625 m	
Si-C sym str		610 s
Ge-C asym str	600 m	
	595 s	
Fe-CO def	575 s	575 s
Ge-C sym str	565 s,sh	
	550 m	560 s

* Cp = (π-C_5H_5)

s = strong; m = medium; w = weak; v = very; sh = shoulder

TABLE XIV

PROTON N.M.R. DATA FOR SOME COMPOUNDS OF 3,3,3-TRIFLUOROPROPYNE

Compound	τ* ($M-CH_3$)	τ* (C_5H_5)	τ* H
$(CH_3)_3GeCHCF_3Fe(CO)_2(\pi-C_5H_5)$	9.7 M = Ge	5.2	2.8 quartet
$(CH_3)_3SiCHCF_3Fe(CO)_2(\pi-C_5H_5)$	9.8 M = Si	5.1	3.0 quartet

* in chloroform

TABLE XV

FLUORINE-19 N.M.R. DATA FOR SOME 3,3,3-TRIFLUOROPROPYNE COMPOUNDS

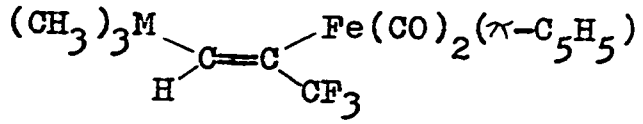
Compound	δ* (p.p.m.)
$(CH_3)_3GeCHCF_3Fe(CO)_2(\pi-C_5H_5)$	59.4 doublet
$(CH_3)_3SiCHCF_3Fe(CO)_2(\pi-C_5H_5)$	60.1 doublet

* in cyclohexane, δ = 0 for external $CFCl_3$

(Table XV), splitting the observed resonance into a doublet.

Although the insertion products are clearly cis isomers, the position of the hydrogen atom and the trifluoromethyl group relative to the silicon (or germanium) atom and the iron atom cannot be assigned unambiguously.

Cullen (81) has shown that a coupling of 1 c.p.s. is observed in the methyl resonance of a trimethyltin or dimethylarsenic group when there is a trifluoromethyl group in geminal position with respect to the tin or arsenic atom (75,81). In the proton n.m.r. spectra of the hexafluorobut-2-yne insertion products discussed earlier, this 1 c.p.s. coupling is observed in the methyl resonance of the trimethylsilicon, trimethylgermanium, or trimethyltin group. The absence of this coupling in the 3,3,3-trifluoropropyne insertion products suggests that the trifluoromethyl group in the product is not geminal to the silicon or germanium atom, and that the structure of these products is:



M= Si, Ge

It is unfortunate that the corresponding tin-iron product was not isolated, since in that case a large ^{119}Sn-C-H coupling should be observed which would determine the structure unambiguously.

CHAPTER VI

EXPERIMENTAL

General

Volatile reagents were manipulated using standard vacuum techniques. Examination of the volatile portion of reaction mixtures was carried out by distillation through a series of cold traps on the vacuum line.

Reactions were carried out in thick-walled Pyrex or silica Carius tubes of about 70 ml capacity. Irradiations in silica tubes were carried out one foot from either a G.E. 400 watt lamp (operating at an equilibrium temperature of 76^{o}) or a Hanovia 200 watt lamp at room temperature.

Microanalyses of products were carried out by Schwartzkopf Microanalytical Laboratory, Woodside 77, N.Y., U.S.A.; Dr. Alfred Bernhardt, Mikroanalytisches Laboratorium, Max-Planck-Institut Für Kohlenforschung, Mulheim (Ruhr), Germany; or by A.B. Gygli, Microanalytical Laboratory, 329 St. George St., Toronto 5, Ontario, Canada.

Infrared spectra of solids were recorded as nujol mulls, of liquids as neat films, and of gases in a 10 cm gas cell

with KBr windows. The spectra were recorded on a Beckman IR-10 Spectrometer. High resolution spectra of the carbonyl region of compounds were recorded on a Beckman IR-7 Spectrometer in cyclohexane solution.

Proton n.m.r. spectra were recorded on a Varian Associates A-60 spectrometer. Proton chemical shifts were measured relative to chloroform at -7.25 p.p.m.

Fluorine n.m.r. spectra were recorded on a Varian Associated DP-60 or a Varian Associates HA-100 spectrometer. Chemical shifts were measured with respect to fluorotrichloromethane.

Most of the reactions described herein were non-stoichiometric. Usually the metal-metal bonded compound was not completely consumed and varying amounts of intractable white decomposition products were formed. It is not known if these residues were due to the instability of the reaction products, or arose from the reaction of the metal-metal bonded compound with traces of oxygen or water.

Extractions were carried out in a nitrogen-filled glove bag. The extract was filtered through a long-stemmed sintered glass filter, and evaporated down by drawing dry nitrogen through the filtering apparatus.

Chromatographic separations were carried out on B.D.H. silica gel (60-120 mesh).

Solvents used were of standard "Reagent" grade, with the exception of hexane, which was redistilled Philips "Technical" grade.

Fluoro-olefins were supplied by Peninsular ChemResearch Inc., Gainseville, Florida, U.S.A., unless otherwise stated.

Trimethyltin chloride was donated by M & T Chemicals, Inc., Rahway, N.J., U.S.A.

II Preparation of Metal-Metal Bonded Compounds

1) Preparation of Trimethyltin(cyclopentadienyl)iron Dicarbonyl

Trimethyltin(cyclopentadienyl)iron dicarbonyl was prepared by the method of Gorsich (4). The sodium salt of cyclopentadienyl iron dicarbonyl was prepared from sodium (3g, 1.13 moles), cyclopentadienyl iron dicarbonyl dimer (10.6g, 0.03 moles, Alfa Inorganics) and mercury (300g) in a three-necked flask containing dry tetrahydrofuran (250 ml) and fitted with a nitrogen inlet and a side arm. The solution was stirred overnight and the excess amalgam drained off. Trimethyltin chloride (10.3g, 52 mmole, M & T Chemicals) was added, and the mixture stirred for two hours, after which the tetrahydrofuran was removed under vacuum. The flask was placed in a nitrogen-filled glove bag and extracted with dichloromethane. The extract was centrifuged, filtered and evaporated down under a nitrogen stream. Distillation at 70-75^{o} and 10^{-3} mm pressure yielded 14.5g of red trimethyltin(cyclopentadienyl)iron dicarbonyl (82% yield, based on trimethyltin chloride).

(Anal. Calcd. for $C_{10}H_{14}O_2FeSn$: C, 35.24; H, 4.11.

Found: C, 35.96; H, 4.42%.)

The compound is a red liquid, stable indefinitely in the absence of air; decomposition following exposure to air is auto-catalytic.

2) Preparation of Trimethylgermanium(cyclopentadienyl)iron Dicarbonyl

Tetramethylgermane was prepared from germanium tetrachloride by methylation according to the method of Hota and Willis (43), and was brominated to give trimethylbromogermane according to the method of Cotton, Tsai, and Clark (13).

Trimethylgermanium(cyclopentadienyl)iron dicarbonyl was prepared by the method used above for the tin analogue. Cyclopentadienyl iron dicarbonyl dimer (8.0g, 23 mmole, Alfa Inorganics), trimethylbromogermane (7.9g, 40 mmole), sodium (2.3g, 0.10 mole) and mercury (230g) yielded 6.5g (56% based on trimethylbromogermane) of red, waxy trimethylgermanium-(cyclopentadienyl)iron dicarbonyl (m. pt. 58-61° after sublimation at 85° and 10^{-3} mm pressure). (Anal. Calcd. for $C_{10}H_{14}O_2GeFe$: C, 40.76; H, 4.76. Found: C, 40.64; H, 4.91%.) The compound is stable indefinitely in the absence of air, but solutions are rapidly oxidized.

3) Preparation of Trimethylsilicon(cyclopentadienyl)iron Dicarbonyl

Trimethylsilicon(cyclopentadienyl)iron dicarbonyl was prepared by the method of Piper and Wilkinson (82).

Cyclopentadienyl iron dicarbonyl dimer (14g, 0.04 mole, Pressure Chemical Company, Pittsburgh, Pennsylvania, U.S.A.), trimethylchlorosilane (25 ml, Alfa Inorganics), sodium (2g, 0.08 mole) and mercury (400g) yielded 13g (70% based on cyclopentadienyl iron dicarbonyl dimer) of orange, waxy trimethylsilicon(cyclopentadienyl)iron dicarbonyl (m. pt. 62-64°) after sublimation at 60° and 10^{-3} mm pressure. (Anal. Calcd. for $C_{10}H_{14}O_2SiFe$: C, 48.02; H, 5.6. Found: C, 48.14; H, 5.6%.)

III Reactions of Metal-Metal Bonded Compounds with Halogens

1) Chlorine with Trimethyltin(cyclopentadienyl)iron Dicarbonyl

a. The tin-iron compound (0.45g, 0.75 mmole) and chlorine (6 mmole, Matheson, Whitby, Ontario) were sealed in a Pyrex Carius tube with carbon tetrachloride (45 ml) and stored at 0° for 15 minutes. The yellow solution turned red immediately.

Carbon monoxide (0.3 mmole) was formed. The volatiles were removed and the residue extracted first with hexane, then with dichloromethane. The hexane extract contained the tin-iron compound (50 mg, 20% recovery). The dichloromethane extract contained cyclopentadienyl iron dicarbonyl chloride, identified by comparison of the infared and n.m.r. spectra with those of a genuine sample prepared by the method of Pauson and Wilkinson (83).

Trimethyltin chloride, identified by its n.m.r. spectrum

(84) was present in the volatile portion of the reaction products.

A considerable amount of insoluble residue remained in the Carius tube.

b. The tin-iron compound (0.35g, 10 mmole) and chlorine (1.2 mmole, Matheson) were sealed in a Pyrex Carius tube with pentane (10 ml) and kept in the dark at -78^{o} for three hours.

The volatiles were removed and the residue extracted first with hexane, then with dichloromethane. The hexane extract contained a trace of the tin-iron compound. The dichloromethane extract gave a red solid, identified as cyclopentadienyl iron dicarbonyl chloride (Anal. Calcd. for $C_8H_5O_2ClFe$: C, 39.58; H, 2.47. Found: C, 39.52; H, 2.67%.)

Trimethyltin chloride, identified by its n.m.r. spectrum, was isolated from the -23^{o} trap of the vacuum system.

2) Iodine with Trimethyltin(cyclopentadienyl)iron Dicarbonyl

a. Iodine (0.16g, 0.62 mmole, A.R.) and the tin-iron compound (0.27g, 0.8 mmole) were refluxed in carbon tetrachloride for thirty minutes.

The reaction vessel contained a black solid, identified as cyclopentadienyl iron dicarbonyl iodide by comparison of its infared and n.m.r. spectra with those of a genuine sample (85).

Trimethyltin chloride, identified by its n.m.r. spectrum, was present in the volatiles (84).

b. Iodine (0.19g, 0.78 mmole) and the tin-iron compound (0.26g, 0.78 mmole) were sealed in a Pyrex Carius tube with pentane (10 ml) and heated for two hours at 60°.

The volatiles were removed to the vacuum system. The Carius tube contained a small amount of the tin-iron compound in addition to cyclopentadienyl iron dicarbonyl iodide (Anal. Calcd. for $C_8H_5O_2FeI$: C, 27.66; H, 1.65. Found: C, 27.48; H, 1.47%.)

3) Iodine Monochloride with Trimethyltin(cyclopentadienyl)-iron Dicarbonyl

Iodine monochloride (0.14g, 0.88 mmole) and the tin-iron compound (0.30g, 0.88 mmole) were refluxed in cyclohexane (5 ml) for thirty minutes.

The volatiles were removed and the residue extracted first with hexane, then with dichloromethane. The hexane extract was the tin-iron compound (40 mg, 12% recovery). The dichloromethane extract (310 mg) was largely cyclopentadienyl iron dicarbonyl iodide, identified spectroscopically. The infared spectrum of this extract contained evidence of a product resulting from replacement of methyl groups on the tin-iron compound by halogen.

The volatile portion of the reaction products contained a mixture of trimethyltin chloride and trimethyltin

iodide. The n.m.r. spectrum of such a mixture has a single broadened resonance between the resonances for pure trimethyltin chloride and pure trimethyltin iodide (86). The position of this resonance is a linear function of the relative concentration of the two tin halides. In the mixture obtained, the observed resonance was at 0.68 p.p.m. downfield from T.M.S., indicating a ratio of trimethyltin chloride to trimethyltin iodide of 3:1.

4) Chlorine with Trimethylgermanium(cyclopentadienyl)-iron Dicarbonyl

Chlorine (0.85 mmole, Matheson) and the germanium-iron compound (0.25g, 0.85 mmole) were sealed in a Pyrex Carius tube and left at 0° overnight.

Carbon monoxide (0.45 mmole) was formed. The volatiles were removed and the residue extracted first with hexane, then with dichloromethane. The hexane extract gave a trace of the germanium-iron compound. The dichloromethane extract contained cyclopentadienyl iron dicarbonyl chloride, identified spectroscopically.

Trimethylchlorogermane, identified by its infared and n.m.r. spectra, was present in the volatiles (84,87).

5) Iodine Monochloride with Trimethylgermanium(cyclopentadienyl)iron Dicarbonyl

Iodine monochloride (0.11g, 0.66 mmole) and the germanium-iron compound (0.18g, 0.62 mmole) were refluxed in

cyclohexane (3 ml) for thirty minutes.

The volatiles were removed and the residues extracted first with hexane, then with dichloromethane. Both extracts contained cyclopentadienyl iron dicarbonyl iodide (160 mg, 86%), identified spectroscopically.

The volatile portion of the reaction products contained trimethylchlorogermane and trimethyliodogermane in a ratio of 3:1, as shown by integration of the n.m.r. spectrum (84).

6) Chlorine with Trimethylsilicon(cyclopentadienyl)iron Dicarbonyl

Chlorine (1.4 mmole, Matheson) and the silicon-iron compound (0.30g, 1.3 mmole) were sealed in a Pyrex Carius tube with chloroform (5 ml) and left overnight at 0°.

Carbon monoxide (0.4 mmole) was formed. The volatiles were removed. The tube contained cyclopentadienyl iron dicarbonyl chloride, identified spectroscopically, and a trace of the silicon-iron compound.

Trimethylchlorosilane, identified by its n.m.r. spectrum (84), was present in the volatiles.

7) Iodine Monochloride with Trimethylsilicon(cyclopentadienyl)iron Dicarbonyl

Iodine monochloride (0.30g, 1.8 mmole) and the silicon-iron compound (0.45g, 1.8 mmole) were refluxed in cyclohexane (5 ml) for thirty minutes.

The volatiles were removed and the residues extracted first with hexane, then with dichloromethane. The hexane extract was the silicon-iron compound (0.15g, 33% recovery). The dichloromethane extract was cyclopentadienyl iron dicarbonyl iodide (0.28g, 51% yield), identified spectroscopically.

The volatile portion of the reaction products contained trimethylchlorosilane, identified by its n.m.r. spectrum (84).

IV Reaction of Metal-Metal Bonded Compounds with Hydrogen Chloride

1) Hydrogen Chloride with Trimethyltin(cyclopentadienyl)-iron Dicarbonyl

a. Anhydrous hydrogen chloride was bubbled through a solution of the tin-iron compound (0.5g, 1.5 mmole) in dichloromethane for ten minutes.

The non-volatile contents of the reaction vessel were chromatographed on silica gel with dichloromethane as eluent. The first fraction gave a yellow oil which decomposed on evaporation of the solvent. The second band was eluted to give a yellow semi-solid, identified as dimethylchlorotin(cyclopentadienyl)iron dicarbonyl (Anal. Calcd. for $C_9H_{11}O_2ClFeSn$: C, 29.92; H, 3.09. Found: C, 29.76; H, 2.75%.)

Trimethyltin chloride, identified by its n.m.r. spectrum (84), was present in the volatiles.

b. Anhydrous hydrogen chloride (4 mmole) and the tin-iron compound (0.7g, 2 mmole) were sealed in a Pyrex Carius tube with dichloromethane (10 ml) and heated to 50° for thirty minutes.

Both methane and carbon monoxide were present in the non-condensible products of the reaction. The non-volatile material in the reaction vessel was chromatographed on silica gel with dichloromethane as eluent. The fraction was collected in a flask immersed in a -78° bath, and the solvent rapidly removed. The remaining yellow oil decomposed at room temperature.

Trimethyltin chloride and unreacted hydrogen chloride were detected in the volatile products of the reaction (identified spectroscopically).

Successive reactions yielded products which were not spectroscopically identical. No attempt was made to obtain elemental analyses.

2) Hydrogen Chloride with Trimethylgermanium(cyclopentadienyl)iron Dicarbonyl

Anhydrous hydrogen chloride (1.4 mmole) and the germanium-iron compound (0.4g, 1.4 mmole) were sealed in a Pyrex Carius tube with dichloromethane (5 ml). After one hour in an oven at 60°, the volatiles were removed from the tube. No methane or excess hydrogen chloride were detected.

The volatiles contained trimethylchlorogermane, identified by its infared and n.m.r. spectra (84,87). The

material in the Carius tube was chromatographed on silica gel with dichloromethane as eluent. The first fraction gave a mixture of the germanium-iron compound and cyclopentadienyl iron dicarbonyl hydride, identified spectroscopically (88). The second fraction gave cyclopentadienyl iron dicarbonyl dimer, identified spectroscopically (89).

3) Hydrogen Chloride with Trimethylsilicon(cyclopentadienyl)iron Dicarbonyl

a. Anhydrous hydrogen chloride was bubbled through a solution of the silicon-iron compound in dichloromethane (15 ml). No reaction occurred.

b. Anhydrous hydrogen chloride (1.4 mmole) and the silicon-iron compound (0.35g, 1.4 mmole) were sealed in a Pyrex Carius tube with dichloromethane (5 ml). After the tube was heated in an oven at 60° for one hour, the tube was opened and the volatiles were removed.

Carbon monoxide (0.7 mmole) was formed. The volatiles contained trimethylchlorosilane, identified by its infared and n.m.r. spectra (84,90).

The material in the Carius tube was chromatographed on silica gel with dichloromethane as eluent. The first fraction yielded a mixture of cyclopentadienyl iron dicarbonyl hydride, identified spectroscopically (88), and the silicon-iron compound. The second fraction was cyclopentadienyl iron dicarbonyl dimer (15 mg, 4%), identified

spectroscopically (89).

c. Anhydrous hydrogen chloride (3 mmole) and the silicon-iron compound (0.5g, 2 mmole) were sealed in a Pyrex Carius tube with dichloromethane (5 ml). After the tube was heated for one hour in an oven at 60°, the volatiles were removed. The cyclopentadienyl iron dicarbonyl hydride was condensed into the -23° trap of the vacuum system, and identified by its n.m.r. spectrum (88). When the solvent was removed, the remaining yellow oil decomposed (with evolution of gas) to give a purple solid, identified as cyclopentadienyl iron dicarbonyl dimer (Anal. Calcd. for $C_{14}H_{10}O_2Fe_2$: C, 47.51; H, 2.83. Found: C, 47.67; H, 2.84%.)

The material in the Carius tube was chromatographed on silica gel with dichloromethane as eluent, to give red, solid cyclopentadienyl iron dicarbonyl dimer (Anal. Calcd. for $C_{14}H_{10}O_2Fe_2$: C, 47.51; H, 2.83. Found: C, 47.45; H, 2.66%.)

If the Carius tube was allowed to stand at room temperature overnight, the yield of cyclopentadienyl iron dicarbonyl dimer increased and the yield of cyclopentadienyl iron dicarbonyl hydride decreased.

V Reactions of Metal-Metal Bonded Compounds with Trifluoroiodomethane

1) Trifluoroiodomethane with Trimethyltin(cyclopentadienyl)-iron Dicarbonyl

a. Trifluoroiodomethane (1.1 mmole) and the tin-iron compound (0.38g, 1.1 mmole) were sealed in a Pyrex Carius tube with carbon tetrachloride (10 ml) and heated at 80° for 12 hours.

Carbon monoxide (0.6 mmole) was formed. The volatiles were removed. The residues were extracted first with hexane, then with chloroform. The hexane extract contained a yellow grease which was not identified. The chloroform extract contained cyclopentadienyl iron dicarbonyl iodide, identified spectroscopically.

A considerable amount of insoluble residue remained in the Carius tube.

b. The tin-iron compound (0.80g, 2.3 mmole) was sealed in a Pyrex Carius tube with enough trifluoroiodomethane to act as solvent and heated at 60° for seven hours. The tube contained a grey solid under a black solution.

The volatiles of the reaction were removed and the residues extracted first with hexane, then with dichloromethane. The hexane extract contained the tin-iron compound (0.4g, 50% recovery). The dichloromethane extract gave a mixture of trifluoromethyl(cyclopentadienyl)iron dicarbonyl

and cyclopentadienyl iron dicarbonyl iodide. It was not possible to effect complete separation of these two compounds by chromatography or by crystallization.

The former compound was less soluble in hexane (Anal. Calcd. for $C_8H_5F_3O_2Fe$: C, 39.06; H, 2.04. Found: C, 37.56; H, 2.03%.) Only cyclopentadienyl iron dicarbonyl iodide was eluted when the mixture was chromatographed on silica gel or alumina with dichloromethane as eluent.

The residue which was insoluble in dichloromethane contained trimethyltir fluoride (100 mg, 20%), identified by its infared spectrum.

The -23^{o} trap of the vacuum system contained trimethyltin iodide (200 mg, 30%), identified by its n.m.r. spectrum (84).

c. The tin-iron compound (0.4g, 1.2 mmole) was sealed in a silica Carius tube with trifluoroiodomethane (5g) and irradiated with ultraviolet light for two hours. The volatiles were removed and the residues extracted first with hexane, then with dichloromethane. The hexane extract contained the tin-iron compound (100 mg, 25% recovery). According to the infared spectrum, the dichloromethane extract contained a mixture of trifluoromethyl(cyclopentadienyl)-iron dicarbonyl and cyclopentadienyl iron dicarbonyl iodide in equal amounts.

The residue which was insoluble in dichloromethane contained trimethyltin fluoride (50 mg, 20%), identified

by its infared spectrum (91).

The -23^{o} trap of the vacuum system contained trimethyltin iodide, identified by its n.m.r. spectrum (84).

2) Trifluoroiodomethane with Trimethylgermanium(cyclopentadienyl)iron Dicarbonyl

The germanium-iron compound (0.50g, 1.7 mmole) was sealed in a Pyrex Carius tube with trifluoroiodomethane (5g) and heated at 80^{o} for 40 hours.

The non-volatile material in the tube was extracted first with hexane, then with dichloromethane. The hexane extract contained the germanium-iron compound. Infrared spectra showed that the dichloromethane extract contained equal amounts of trifluoromethyl(cyclopentadienyl)iron dicarbonyl and cyclopentadienyl iron dicarbonyl iodide.

The volatiles contained equal amounts of trimethyliodogermane and trimethylfluorogermane, as shown by integration of the n.m.r. spectrum.

3) Trifluoroiodomethane with Trimethylsilicon(cyclopentadienyl)iron Dicarbonyl

The silicon-iron compound (0.50g, 2 mmole) was sealed in a Pyrex Carius tube with trifluoroiodomethane (10g) and heated at 80^{o} for 90 hours.

The non-volatile material in the tube was extracted first with hexane, then with dichloromethane. The hexane extract was the silicon-iron compound (200 mg, 40% recovery).

The dichloromethane extract gave cyclopentadienyl iron dicarbonyl iodide (100 mg, 25% yield), identified spectroscopically.

The volatile portion of the reaction contained trimethylfluorosilane, identified by its n.m.r. spectrum (84).

VI Reactions of Metal-Metal Bonded Compounds with Sulfur Dioxide

1) Sulfur Dioxide with Trimethyltin(cyclopentadienyl)iron Dicarbonyl

Sulfur dioxide (5 ml, Matheson, anhydrous) and the tin-iron compound (0.5g, 1.5 mmole) were sealed in a Pyrex Carius tube. After the tube was shaken for five hours, the volatiles were removed.

The residue was extracted with dichloromethane. The extract yielded a brown solid (m. pt. 80+^{o}, with gas evolution) which was isolated in essentially quantitative yield. (Anal. Calcd. for $C_{10}H_{14}O_5S_{1.5}FeSn$: C, 27.49; H, 3.2; S, 11.00. Found: C, 25.45; H, 3.49; S, 10.89%.)

2) Sulfur Dioxide with Trimethylgermanium(cyclopentadienyl)-iron Dicarbonyl

Sulfur dioxide (5g, Matheson) and the germanium-iron compound (0.25g, 0.85 mmole) were sealed in a Pyrex Carius tube. After the tube was shaken for six hours, the volatiles were removed.

The residue was extracted with dichloromethane yielding a brown solid. After repeated recrystallization from a hexane/dichloromethane mixture, yellow crystals were obtained (200 mg, 80% yield, m. pt. 148-149° with decomposition). (Anal. Calcd. for $C_{10}H_{14}O_4SGeFe$: C, 33.48; H, 3.91; S, 8.92. Found: C, 32.36; H, 3.71; S, 8.35%.)

3) Sulfur Dioxide with Trimethylsilicon(cyclopentadienyl)-iron Dicarbonyl

a. Sulfur dioxide (5g) and the silicon-iron compound (0.50g, 2 mmole) were sealed in a Pyrex Carius tube. After the tube was shaken for six hours, the volatiles were removed.

The hexane extract of the residues contained only unchanged silicon-iron compound.

b. Sulfur dioxide (5 ml) and the silicon-iron compound (0.50 g, 2 mmole) were sealed in a Pyrex Carius tube and heated at 76° for 24 hours.

Carbon monoxide (0.9 mmole) was formed. The residue was extracted with dichloromethane. No identifiable product could be crystallized from the tar formed in the reaction. One half of the material in the tube was a shiny black solid, sparingly soluble in methanol. The infrared spectrum of this material contained no peaks characteristic of the silicon-iron compound.

VII Reactions of Metal-Metal Bonded Compounds with Hexafluorobut-2-yne

1) Hexafluorobut-2-yne with Trimethyltin(cyclopentadienyl)-iron Dicarbonyl

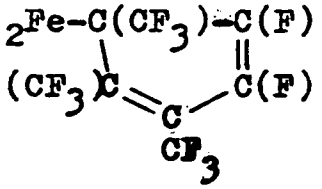
a. Hexafluorobut-2-yne (13 mmole) and the tin-iron compound (1.4g. 4 mmole) were sealed in a silica Carius tube with hexane (10 ml) and irradiated for 84 hours. The solution in the tube turned black.

The reaction volatiles were removed and the residues extracted with hexane. The extract was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction contained the tin-iron compound (0.55g, 40% recovery). The second fraction gave a yellow solid (0.12g, 15% yield, m.pt. 86-88° after recrystallization from pentane), formulated as $(CH_3)_3SnC(CF_3)=C(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$. (Anal: Calc'd for $C_{14}H_{14}O_2F_6FeSn$: C, 33.43; H, 2.78. Found: C, 33.42; H, 2.77%). The infared spectra indicated that successive fractions contained increasing amounts of fluorocarbon polymer.

b. Hexafluorobut-2-yne (12 mmole) and the tin-iron compound (1.5g, 4.5 mmole) were sealed in a silica Carius tube with hexane (10 ml) and irradiated for 40 hours at 76°.

Carbon monoxide (1.7 mmole) was formed. The reaction volatiles were removed and the residues extracted with hexane.

The extract was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction contained the tin-iron compound (0.5g, 30% recovery) as well as some of the 1:1 insertion product, which was identified spectroscopically. The second fraction gave a mixture of two fluorocarbon compounds of iron (250 mg, 15%). This mixture was again chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction gave a yellow powder, <u>trans</u>-$H(CF_3)C{=}C(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$ (m. pt. 37.5-39°, <u>Anal</u>: Calc'd for $C_{11}H_6O_2F_6Fe$: C, 38.85; H, 1.76; F, 33.55. Found: C, 38.82; H, 1.92; F, 33.89%.) The second fraction gave a yellow, waxy solid (m. pt. 40-42°): formulated as



(<u>Anal</u>: Calc'd. for $C_{15}H_5O_2F_{11}Fe$: C, 37.36; H, 1.04; F, 43.38. Found: C, 37.00; H, 1.08; F, 42.77%.)

The dichloromethane-insoluble residue contained trimethyltin fluoride (165 mg, 20%), identified by its infared spectrum (91).

The volatile fraction of the reaction products contained tetramethyltin, identified by its n.m.r. spectrum (92).

2) Hexafluorobut-2-yne with Trimethylgermanium(cyclopentadienyl)iron Dicarbonyl

a. Hexafluorobut-2-yne (10 mmole) and the germanium-iron compound (0.75g, 2.5 mmole) were sealed in a silica Carius tube with hexane (5 ml) and irradiated for 46 hours at 25°.

Carbon monoxide (0.5 mmole) was formed. The reaction volatiles were removed and the residues extracted with hexane. The extract was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction contained the germanium-iron compound (0.40g, 55% recovery). The second fraction gave a yellow solid, (50 mg, 4% yield, m. pt. 83-85°).

The volatile portion of the reaction products contained trimethylfluorogermane, identified by its infared and n.m.r. spectra (13,84).

b. Hexafluorobut-2-yne (12 mmole) and the germanium-iron compound (1.0g, 3.5 mmole) were sealed in a silica Carius tube with hexane (10 ml) and irradiated for 42 hours at 76°.

Carbon monoxide (0.7 mmole) was formed. The reaction volatiles were removed and the residues extracted with hexane. The extract was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction contained the germanium-iron compound (0.60g, 60% recovery). The second fraction contained the 1:1 insertion product $(CH_3)_3GeC(CF_3)=C(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$, (175 mg, 15%). (Anal. Calcd. for $C_{14}H_{14}O_2F_6GeFe$: C, 36.81; H, 3.06; F, 24.98.

Found: C, 36.63; H, 3.14; F, 25.83%.)

The volatile portion of the reaction products contained trimethylfluorogermane and tetramethylgermane, identified by their n.m.r. spectra (84,92).

c. Hexafluorobut-2-yne (3 mmole) and the 1:1 butyne insertion product (75 mg, 1.7 mmole) were sealed in a silica Carius tube with hexane (5 ml) and irradiated for 20 hours at 76°.

Carbon monoxide (0.18 mmole) was formed. The reaction volatiles were removed and the hexane extract of the residues was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction gave the 1:1 butyne insertion product (28 mg, 37% recovery), identified spectroscopically. The infrared spectra showed that subsequent fractions contained increasing amounts of fluorocarbon polymer.

3) Hexafluorobut-2-yne with Trimethylsilicon(cyclopentadienyl)iron Dicarbonyl

a. Hexafluorobut-2-yne (15 mmole) and the silicon-iron compound (0.75g, 3 mmole) were sealed in a silica Carius tube with hexane (5 ml) and irradiated for 43 hours at 25°.

Carbon monoxide (0.4 mmole) was formed. The reaction volatiles were removed. The hexane extract of the residues was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction contained the silicon-iron compound (0.52g, 70% recovery). The second fraction

gave a yellow solid (50 mg, 4% yield, m. pt. 78-81°).

b. Hexafluorobut-2-yne (12 mmole) and the silicon-iron compound (0.75g, 3 mmole) were sealed in a silica Carius tube with hexane (5 ml) and irradiated for 43 hours at 76°.

Carbon monoxide (0.8 mmole) was formed. The reaction volatiles were removed. The hexane extract of the residues was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction contained the silicon-iron compound (0.40g, 50% recovery). The second fraction gave a yellow solid, $(CH_3)_3SiC(CF_3)=C(CF_3)Fe(CO)_2(\pi-C_5H_5)$ (100 mg, 8% yield). (Anal. Calcd. for $C_{14}H_{14}O_2F_6FeSI$: C, 40.79; H, 3.4; F, 27.68. Found: C, 41.59; H, 3.48; F, 27.00%.) The infrared spectra showed that subsequent fractions contained increasing amounts of fluorocarbon polymer.

Trimethylfluorosilane and tetramethylsilane, identified by their n.m.r. spectra (84,92), were found in the volatile fraction of the reaction products.

VIII Reactions of Metal-Metal Bonded Compounds with 3,3,3-Trifluoropropyne

1) 3,3,3-Trifluoropropyne with Trimethyltin(cyclopentadienyl)iron Dicarbonyl

a. 3,3,3-Trifluoropropyne (11 mmole), prepared by the method

of Finnegan and Norris (93), and the tin-iron compound (1.0 g, 3 mmole) were sealed in a silica Carius tube with hexane (5 ml) and irradiated for 30 hours at 25°.

Carbon monoxide (1.6 mmole) was formed. The reaction volatiles were removed. The hexane extract of the residues was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction contained the tin-iron compound (0.15 g, 15% recovery). The second fraction gave a yellow oil, cis-$H(CF_3)C{=}C(H)Fe(CO)_2(\pi\text{-}C_5H_5)$, ((50 mg, 5% yield). (Anal: Calcd. for $C_{10}H_7O_2F_3Fe$: C,44.15; H, 2.57; F, 20.97. Found: C,43.88; H, 2.54; F, 23.21 and 19.67%.) The infrared spectra showed that subsequent fractions contained increasing amounts of fluorocarbon polymer.

Examination of the volatile fraction of the reaction products indicated that approximately one third (3 mmole) of the propyne had been consumed.

b. 3,3,3-Trifluoropropyne (10 mmole) and the tin-iron compound (0.75 g, 2.2 mmole) were sealed in a Pyrex Carius tube with hexane (5 ml) and heated for 84 hours at 80°.

The tin-iron compound was recovered unchanged.

2) 3,3,3-Trifluoropropyne with Trimethylgermanium(cyclopentadienyl)iron Dicarbonyl

a. 3,3,3-Trifluoropropyne (15 mmole) and the germanium-iron compound (0.75 g, 2.5 mmole) were sealed in a silica Carius tube with hexane (10 ml) and irradiated for 24 hours

at 25°.

Carbon monoxide (0.1 mmole) was formed. The reaction volatiles were removed. The hexane extract of the residues was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction contained the germanium-iron compound (100 mg, 15% recovery). The second fraction gave a yellow oil (60 mg, 7% yield), formulated as $(CH_3)_3GeC_2H(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$. (Anal: Calcd. for $C_{13}H_{15}O_2F_3GeFe$: C, 40.16; H, 3.86; F, 14.68 Found: The infared spectra showed that subsequent fractions contained increasing amounts of fluorocarbon polymer.

Examination of the volatile fraction of the reaction procucts indicated that approximately one quarter (3 mmole) of the propyne had been consumed.

b. 3,3,3-Trifluoropropyne (12 mmole) and the germanium-iron compound (0.75 g, 2.5 mmole) were sealed in a silica Carius tube with hexane (10 ml) and irradiated for 48 hours at 76°.

Carbon monoxide (1 mmole) was formed. The reaction volatiles were removed. The hexane extract of the residues was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction contained the germanium-iron compound (75 mg, 10% recovery). The second fraction contained the propyne insertion product (200 mg, 20% yield). Polymerization of the propyne was so extensive that the

product was contaminated.

3) 3,3,3-Trifluoropropyne with Trimethylsilicon(cyclopentadienyl)iron Dicarbonyl

a. 3,3,3-Trifluoropropyne (13 mmole) and the silicon-iron compound (0.75g, 3 mmole) were sealed in a silica Carius tube with hexane (5 ml) and irradiated for 48 hours at 25°.

Carbon monoxide (0.9 mmole) was formed. The reaction volatiles were removed. The hexane extract of the residues in the tube was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction contained the silicon-iron compound (0.22g, 30% recovery). The second fraction gave a yellow oil, $(CH_3)_3SiC_2H(CF_3)Fe(CO)_2(\pi\text{-}C_5H_5)$ (70 mg, 6%) (Anal: Calcd. for $C_{13}H_{15}O_2F_3FeSi$: C, 45.36; H, 4.36; F, 16.57. Found:

b. 3,3,3-Trifluoropropyne (12 mmole) and the silicon-iron compound (0.75g, 3 mmole) were sealed in a silica Carius tube with hexane (5 ml) and irradiated for 48 hours at 76°.

Carbon monoxide (1.7 mmole) was formed. The reaction volatiles were removed. The hexane extract of the residues was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction contained the silicon-iron compound (100 mg, 13% recovery). The second fraction gave a yellow oil, (5 mg, 1%) which was not characterized. The third fraction contained the 1:1 propyne insertion product (100 mg, 11%). The infrared spectra showed that

subsequent fractions contained increasing amounts of fluorocarbon polymer.

Examination of the volatile fraction of the reaction products indicated that approximately one third (4 mmole) of the propyne was consumed. Trimethylfluorosilane was identified by its infrared and n.m.r. spectra (84,94).

IX Reactions of Metal-Metal Bonded Compounds with Perfluorocyclobutene

1) Perfluorocyclobutene with Trimethyltin(cyclopentadienyl)-iron Dicarbonyl

a. Perfluorocyclobutene (16 mmole) and the tin-iron compound (1.0g, 3 mmole) were sealed in a silica Carius tube with hexane (7 ml) and irradiated for 24 hours at 25°.

The tin-iron compound was recovered unchanged.

b. Perfluorocyclobutene (16 mmole) and the tin-iron compound (1.0g, 3 mmole) were sealed in a silica Carius tube with hexane (7 ml) and irradiated for 30 hours at 76°.

The reaction volatiles were removed and the residues in the tube were extracted first with hexane, then with dichloromethane. The hexane extract contained the tin-iron compound. The dichloromethane extract gave cyclopentadienyl iron dicarbonyl dimer, identified spectroscopically.

Sublimation of the dichloromethane-insoluble residue

yielded trimethyltin fluoride (36 mg, 7% yield), identified spectroscopically (91).

2) Perfluorocyclobutene with Trimethylgermanium(cyclopentadienyl)iron Dicarbonyl

Perfluorocyclobutene (10 mmole) and the germanium-iron compound (0.50 g, 1.7 mmole) were sealed in a silica Carius tube with hexane (7 ml) and irradiated for 48 hours at 25°.

The reaction volatiles were removed, and the residues in the tube extracted first with hexane, then with dichloromethane. The hexane extract contained the germanium-iron compound (0.20 g, 40% recovery). The dichloromethane extract gave cyclopentadienyl iron dicarbonyl dimer (55 mg, 18% yield),identified spectroscopically.

Trimethylfluorogermane and some tetramethylgermane, identified spectroscopically (84,92), were present in the volatile fraction of the reaction products.

3) Perfluorocyclobutene with Trimethylsilicon(cyclopentadienyl)iron Dicarbonyl

a. Perfluorocyclobutene (15 mmole) and the silicon-iron compound (0.75 g, 3 mmole) were sealed in a silica Carius tube with hexane (7 ml) and irradiated for 48 hours at 25°.

The reaction volatiles were removed and the residues in the tube extracted first with hexane, then with dichloromethane. The hexane extract was the silicon-iron compound.

The dichloromethane extract gave cyclopentadienyl iron dicarbonyl dimer (75 mg, 14% yield), identified spectroscopically.

b. Perfluorocyclobutene (15 mmole) and the silicon-iron compound (0.75g, 3 mmole) were sealed in a silica Carius tube with acetone (5 ml) and irradiated for 41 hours at 76°.

Carbon monoxide (1.4 mmole) was formed. The reaction volatiles were removed. The hexane extract of the residues in the tube was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction contained the silicon-iron compound (150 mg, 20% recovery). The second fraction gave a yellow powder, which, according to its infrared spectrum, did not contain carbon-fluorine bonds. The third fraction contained a greenish oil, which, according to the infared spectrum, was a fluorocarbon polymer.

The black powder remaining in the Carius tube was insoluble in common organic solvents.

Trimethylfluorosilane, identified by its infared and n.m.r. spectra (84,94), was present in the volatile fraction of the reaction products.

X Reaction of Metal-Metal Bonded Compounds with Trifluoroethylene

1) Trifluoroethylene with Trimethyltin(cyclopentadienyl)-iron Dicarbonyl

a. Trifluoroethylene (15 mmole) and the tin-iron compound (1.0g, 3 mmole) were sealed in a silica Carius tube with hexane (7 ml) and irradiated for 50 hours at 25°.

The reaction volatiles were removed. The residues in the tube were extracted first with hexane, then with dichloromethane. The hexane extract was the tin-iron compound. The dichloromethane extract was cyclopentadienyl iron dicarbonyl dimer, identified spectroscopically.

b. Trifluoroethylene (15 mmole) and the tin-iron compound (1.0g, 3 mmole) were sealed in a silica Carius tube with tetrahydrofuran (7 ml) and irradiated for 51 hours at 76°.

Carbon monoxide (0.7 mmole) was formed. The reaction volatiles were removed and the residues extracted first with hexane, then with dichloromethane. The dichloromethane extract was cyclopentadienyl iron dicarbonyl dimer, identified spectroscopically. The hexane extract was chromatographed on silica gel with a hexane/benzene mixture as eluent. The only fraction contained a yellow powder (30mg, 3%), which, according to the infrared spectrum, did not contain carbon-fluorine bonds.

c. Trifluoroethylene (15 mmole) and the tin-iron compound (1.0 g, 3 mmole) were sealed in a silica Carius tube with tetrahydrofuran (7 ml) and irradiated for 24 hours at 76°.

Carbon monoxide (1.0 mmole) was formed. The reaction volatiles were removed and the residues extracted with hexane. The extract was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction contained the tin-iron compound (30 mg, 3% recovery). The second fraction contained a yellow powder (30 mg, 3% yield), which, according to the infrared spectrum, did not contain carbon-fluorine bonds. The third fraction gave a yellow oil (45 mg, 4% yield). Spectroscopic investigation of this oil indicated that it contained at least three different compounds. No attempt was made at separation because of the extremely small amounts involved.

2) <u>Trifluoroethylene with Trimethylgermanium(cyclopentadienyl)iron Dicarbonyl</u>

a. Trifluoroethylene (10 mmole) and the germanium-iron compound (0.50 g, 1.7 mmole) were sealed in a silica Carius tube with hexane (7 ml) and irradiated for 45 hours at 76°.

Carbon monoxide (0.4 mmole) was formed. The volatiles were removed and the residues extracted first with hexane, then with dichloromethane. The hexane extract gave unchanged germanium-iron compound. The methylene chloride extract contained a trace of cyclopentadienyl iron dicarbonyl dimer, identified spectroscopically.

b. Trifluoroethylene (10 mmole) and the germanium-iron compound (0.50g, 1.7 mmole) were sealed in a silica Carius tube with hexane (7 ml) and irradiated for 45 hours at 76°.

Carbon monoxide (1.5 mmole) was formed. The volatiles were removed and the residues extracted first with hexane, then with dichloromethane. The hexane extract was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction contained a yellow powder (5 mg, 1% yield). The second fraction gave a yellow oil (10 mg, 2% yield). These yields were judged to be too low to permit characterization of the products.

Trimethylfluorogermane, identified by its n.m.r. spectrum (84), was present in the volatile fraction of the reaction products.

XI Reactions of Metal-Metal Bonded Compounds with Chlorotrifluoroethylene

1) Chlorotrifluoroethylene with Trimethyltin(cyclopentadienyl)iron Dicarbonyl

Chlorotrifluoroethylene (15 mmole) and the tin-iron compound (1.0g, 3.0 mmole) were sealed in a silica Carius tube with hexane (7 ml) and irradiated for 48 hours at 76°.

Carbon monoxide (0.9 mmole) was formed. The volatiles were removed and the residues extracted first with hexane, then with dichloromethane. The dichloromethane extract was handled with difficulty due to the presence of a grease

(Kel-F?). The hexane extract was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction contained the tin-iron compound (100 mg, 10% recovery). The second fraction gave a yellow oil (20 mg, 2% yield), tentatively identified as $(\pi\text{-}C_5H_5)Fe(CO)_2C(F)=CF_2$ by the infared spectrum. The yield was judged insufficient to permit complete characterization.

The volatile fraction of the reaction products contained trimethyltin chloride (180 mg, 30% yield), identified by its n.m.r. spectrum (84).

Sublimation of the dichloromethane-insoluble residue afforded trimethyltin fluoride (11 mg, 2% yield), identified by the infared spectrum (91).

2) Chlorotrifluoroethylene with Trimethylgermanium(cyclopentadienyl)iron Dicarbonyl

Chlorotrifluoroethylene (10 mmole) and the germanium-iron compound (0.50g, 1.7 mmole) were sealed in a silica Carius tube with hexane (7 ml) and irradiated for 48 hours at 76°.

Carbon monoxide (0.9 mmole) was formed. The volatiles were removed. The hexane extract of the residues was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction contained the germanium-iron compound (5 mg, 1% recovery). The second fraction gave a yellow oil (5 mg, 1% yield). The low yield prevented its characterization.

The volatile fraction of the reaction products contained trimethylchlorogermane, as well as some trimethylfluorogermane, both identified by their n.m.r. spectra (84).

3) Chlorotrifluoroethylene with Trimethylsilicon(cyclopentadienyl)iron Dicarbonyl

Chlorotrifluoroethylene (15 mmole) and the silicon-iron compound (0.75 g, 3 mmole) were sealed in a silica Carius tube with hexane (7 ml) and irradiated for 48 hours at 76°.

Carbon monoxide (0.7 mmole) was formed. The volatiles were removed and the residues extracted with hexane. The extract was chromatographed on silica gel with a hexane/benzene mixture as eluent. The first fraction contained the silicon-iron compound (0.25 g, 33% recovery). The second fraction gave a yellow oil (40 mg, 5% yield), tentatively identified as $(\pi\text{-}C_5H_5)Fe(CO)_2C(F)=CF_2$ by the infared spectrum.

The volatiles contained equal amounts of trimethylchlorosilane and trimethylfluorosilane, as shown by integration of the n.m.r. spectrum (84).

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